

Groundwater age, life expectancy and transit time distributions in advective–dispersive systems:1. Generalized Reservoir Theory.

F. Cornaton*, P. Perrochet

CHYN, Institute of Geology, University of Neuchâtel, Emile-Argand 11, CH-2007, Neuchâtel, Switzerland

Abstract

We present a methodology for determining reservoir groundwater age and transit time probability distributions in a deterministic manner, considering advective–dispersive transport in steady velocity fields. In a first step, we propose to model the statistical distribution of groundwater age at aquifer scale by means of the classical advection–dispersion equation for a conservative and non-reactive tracer, associated to proper boundary conditions. The evaluated function corresponds to the density of probability of the random variable age, age being defined as the time elapsed since the water particles entered the aquifer. An adjoint backward model is introduced to characterize the life expectancy distribution, life expectancy being the time remaining before leaving the aquifer. By convolution of these two distributions, groundwater transit time distributions, from inlet to outlet, are fully defined for the entire aquifer domain. In a second step, an accurate and efficient method is introduced to simulate the transit time distribution at discharge zones. By applying the reservoir theory to advective–dispersive aquifer systems, we demonstrate that the discharge zone transit time distribution can be evaluated if the internal age probability distribution is known. The reservoir theory also applies to internal life expectancy probabilities yielding the recharge zone life expectancy distribution. Internal groundwater volumes are finally identified with respect to age and transit time. One- and two-dimensional theoretical examples are presented to illustrate the proposed mathematical models, and make inferences on the effect of aquifer structure and macro–dispersion on the distributions of age, life expectancy and transit time.

Key words: age; life expectancy; transit time; reservoir theory; dispersion; Laplace transforms; finite elements

* Corresponding author.

Email addresses: `fabien.cornaton@unine.ch` (F. Cornaton),
`pierre.perrochet@unine.ch` (P. Perrochet).

1 Introduction.

The knowledge of groundwater age distributions is of prime interest in many environmental issues since they depend on the intrinsic characteristics of the overall transport properties of an aquifer and its sub-systems. For instance, an important fraction of young water within a water sample can often be taken as the signature of a reservoir with good turnover property. On the opposite, a considerable component of old water may reflect a poorly recharged aquifer, and/or significant internal mixing processes. The impact of a contamination hazard on groundwater quality can be investigated using groundwater age, since the age distribution provides direct information on the time required for a water particle, or a conservative tracer, to reach any critical zone that is to be protected. The fate of a solute being transported in groundwater partially depends on the time spent by the water molecules during their migration throughout the aquifer system. Reactive transport of a specific substance is also linked to groundwater age; the time spent flowing through any kind of mineral heterogeneity being a conditional factor for the development of any potential reactions. With the age information, inferences can be made on the aquifer physical characteristics, as well as on the chemical transformations that contaminants may undergo. The age can also be of importance for estimating historical aspects related e.g. to the agricultural practices, or the land use of a particular region, which are expected to have lead to groundwater contamination. As it is the case throughout this work, groundwater age can be considered as a fully conservative tracer. Consequently, the worst scenario with regard to a contamination case is thus chosen by solving the age transport problem.

Generally, a water sample shows a mixture of ages, which may range between several orders of magnitude, as a consequence of the reservoir geometrical and hydro-dispersive characteristics (spatial repartition of the hydraulic and transport parameters). Groundwater age must, therefore, be regarded as a statistical, or probabilistic distribution, rather than considering it as a single absolute or average value. The dating methods commonly provide an average value over the water sample for the age of groundwater after recharge, which in theory does not represent hard data. In fact, the mean of an unknown distribution, here the distribution of ages, is not necessarily a reliable value for the most likely of this distribution. By far the most frequently used dating methods are based on the measurements of natural tracers, such as the isotopes of radon, carbon or oxygen, and on the measurements of man-induced atmospheric concentrations of elements such as tritium (^3H), helium (^3He), chloride (^{36}Cl), krypton (^{85}Kr), or chlorofluorocarbons (CFC), which have increased steadily between the 1940s and the early 1990s. The most efficient methods for dating recent waters are the ones based on $^3\text{H}/^3\text{He}$, ^{85}Kr , and CFC-measurements [63,55,25], which are known to provide age dates over a

period of 40 years with an accuracy of 20% or less [11]. CFC-based ages provide a good resolution for groundwater with relatively young components [8,6], but they do not account for the time spent by water molecules within the unsaturated zone, such that in the case of deep water table aquifers the travel time duration within the unsaturated zone must, therefore, be estimated. Absolute dating techniques involve decay of radionuclides in groundwater, for which ^{14}C or ^{36}Cl are classical elements that are used for dating old groundwater, e.g. in deep and large sedimentary basins. Groundwater age is very often used to make inferences on aquifer parameters, groundwater recharge, flow paths and flow velocities. However, with many of these dating methods, the interpretation of ages is achieved by means of simple conceptual models and fitting the data. This involves significant simplifications of the flow and transport processes, which may lead to erroneous interpretations about e.g. the past release of contaminants in aquifers. As will be discussed in this paper, mixing and dispersion are major factors, which can lead to unrepresentative mean age measurements. Dating methods remain however very useful for calibrating numerical models [56,58], which attempt to simulate the flow patterns, the flow rates, and the distribution of ages in groundwater.

To quantify the distribution of ages in aquifers, several types of mathematical models have been developed during the past decades of research in this field. Nevertheless, in many cases age distributions are more or less arbitrarily chosen and not deterministically calculated. Analytical lumped-parameter type models have been however extensively used in the simulation of environmental tracer data [45,47,74,9,57,1], such as isotopic data, which are commonly interpreted with advective transit time models, although isotope transport does not necessarily undergo advective processes only. Specified transit time distributions describing piston-flow, exponential mixing, combined piston-exponential mixing, or dispersive mixing, are chosen to solve the inverse problem by fitting the model on measured tracer output data. This procedure calls for significant simplifications, which can often not be justified, such as for instance neglecting the reservoir structure, as well as the spatial variability of infiltration rates [10] and aquifer flow and transport parameters. Amin and Campana [1] proposed to model the groundwater age mixing process by means of a three-parameter gamma function which accounts for various states of mixing ranging between no mixing (piston flow model) and perfect mixing (exponential model). Robust verifications of the applicability of lumped parameter models can hardly be found [36,44,28]. Transit time distributions are often obtained with numerical solutions by making the assumption of pure advective motion of the groundwater particles, the particle-tracking technique being the most popular one. Purely kinematic ages ignore the effect of dispersion and mixing on age transport [22,12], and often reveal to be ill posed in complex heterogeneous systems [71], for which the 3-D implementation is subject to severe technical problems. The importance of including age dilution processes such as dispersion and matrix diffusion, when comparison is made between modeled and

measured ages, has been pointed out by many authors [66,45,46]. Moreover, particle-tracking does not allow calculation of transit time distributions since groundwater volumes are not associated to simulated ages.

More elaborated quantitative approaches consider age as a mass that is transported by groundwater through volume-averaged temporal moment equations [64,37,35,71], in which the product of groundwater age with its mass (age mass ρA) is the conserved quantity. Harvey and Gorelick [37], and Varni and Carrera [71] derived a set of recursive temporal moment equations, which are sequentially solved in order to simulate the transit time distributions from the n calculated moments. According to Harvey and Gorelick [37], the first five moments that characterize the accumulated mass, the mean, the variance, the skewness and the kurtosis of a breakthrough curve, respectively, may provide sufficient information to summarize the entire distribution. Since many natural systems reveal a multi-modality of the age distribution within the reservoir and at the discharge zones, and since the shape of this distribution is a priori unknown, an infinity of moments would therefore theoretically be required to construct the entire distribution.

In the literature one can find many terms, which relate to a specific time spent by water molecules within the aquifer. Use will be made throughout this work of the notion of transit time as the total residence time of water molecules within the aquifer, i.e. the age of these molecules when they exit the aquifer. The notion of travel time is rather used to characterize the time spent to travel between two arbitrary locations in the aquifer. Travel time probabilities have been a subject of high interest in many studies characterizing solute transport in sub-surface hydrology [16,18,19,38,39]. The travel time probability is commonly defined as the response function to an instantaneous unit flux impulse [21,39]. In their transfer function approach of contaminant transport through unsaturated soil units, Jury and Roth [39] model tracer breakthrough curves with one-dimensional travel time probability functions. Shapiro and Cvetkovic [60], Dagan [19], and Dagan and Nguyen [20] derived the forward travel time probability for a mass of solute by using the Lagrangian concept of particle displacement in porous media. The derivation of forward and backward models for location and travel time probability has become a classical mathematical approach for contaminant transport characterization and prediction [69,43,50,51]. The spreading of a contaminant mass is analyzed by following the random motion of solute particles, and to do so, the advection–dispersion equation (ADE) is assimilated to the Fokker-Planck (or forward Kolmogorov) equation. The expected resident concentration of a conservative tracer is taken as the probability density function for the location of a particle, at any time after having entered the system.

The aim of the present work is to provide a general theoretical framework to model complete groundwater age distributions at aquifer scale in a determin-

istic way. The concept of age variability is associated to the concept of random variables and their distributions by using classical elements of probability, allowing the introduction of mathematical definitions for age, life expectancy and transit time statistical distributions. Forward and backward ADEs for conservative tracers are used to simulate the above-mentioned distributions at aquifer scale. By manipulating the ADEs, the reservoir theory [27] is expressed in order to characterize recharge and discharge zones transit time distributions with refined accuracy. The proposed models are illustrated and discussed by means of analytical and numerical analysis of one- and two-dimensional theoretical flow configurations.

2 The 'ages' of groundwater as space-dependent random variables.

In this section we present the models allowing the calculation of the statistical distribution of groundwater age, life expectancy and transit time in arbitrary aquifers.

2.1 *Definitions.*

The characterization of groundwater molecules with respect to a travel time within an aquifer system is fully dependent on the spatial reference from which this time is "measured". Usually the groundwater age is defined as a relative quantity with respect to a starting location where age is assumed to be zero. Use will be made throughout this work of three variations of terminology. For a given spatial position in the reservoir, the age (A) relates to the time elapsed since the water molecules entered the system at the recharge limits, where age is zero. For the same spatial position, the life expectancy (E) is defined as the time required for the water molecules to reach an outlet limit of the system. Life expectancy is therefore zero at an outlet. The transit time (T) finally refers to the total time required by the same water molecules to migrate from an inlet zone ($T = E$) to an outlet zone ($T = A$). In a REV, the three variables A , E and T are random variables, characterized by probability density functions (pdf) that can be regarded as the statistical occurrence of water molecules with respect to time, which could be observed in a groundwater sample if any analytical procedure would allow such measurements.

2.2 Age probability.

The typical heterogeneity of aquifer systems involves strongly varying flow velocity fields, with multi-scale coherence lengths. The spatial variability of velocity and transport parameters induces a spreading of the contaminant mass. The tensor of macro-dispersion in the classical ADE accounts for the uncertainty in the transport prediction induced by mixing. Various studies relate to how the ADE is limited by the impact of physical and chemical heterogeneities on solute transport, such that up-scaling is not always satisfying [17,67,34]. If such heterogeneities are present at aquifer scale the transport parameters should be time-dependent, but this time dependency may be relaxed when the correlation scales of the transport parameter random fields are finite [34,49]. The ADE with time-independent parameters holds only when the solute particles have enough time to be distributed by dispersion between the flow lines. Since we are interested in solving the age transport problem at aquifer scale, we make the assumption that the ADE with time-independent transport parameters (the parameters have reached their asymptotic values) can model the evolutionary transport of the groundwater age and life expectancy distributions under steady-flow conditions. The modelled process applies to conservative and non-reactive tracers.

Let us consider an aquifer domain Ω in the three-dimensional space, with hydraulic recharge boundary Γ_- , discharge boundary Γ_+ , and impermeable boundary Γ_0 , as illustrated in Fig. 1. The boundary Γ_+ corresponds to the open boundary of the system, through which a free exit of age mass is expected. With respect to the above-mentioned considerations on contaminant spreading, it is convenient to describe the groundwater sample age distribution as a random variable associated to a probabilistic model. The age probability distribution at a position \mathbf{x} in Ω can be evaluated by solving the ADE when a unit pulse of conservative tracer is uniformly applied on the recharge area Γ_- . The resulting breakthrough curve is the probabilistic age distribution [21,39]. Making use of this property, we propose to model groundwater age and life expectancy pdfs by forward and backward transient-state transport equations, under steady-state hydraulic conditions. The pre-solution of the velocity field is performed by the following steady-state groundwater flow equation:

$$\nabla \cdot \mathbf{q} = q_I - q_O, \quad \mathbf{q} = -\mathbf{K} \nabla H \quad \text{in } \Omega, \quad (1)$$

where \mathbf{q} is the Darcy flux vector [LT^{-1}], which is valid for ideal tracers, H is the hydraulic head [L], q_I and q_O are fluid source and sink terms [T^{-1}], respectively, and \mathbf{K} is the tensor of hydraulic conductivity [LT^{-1}]. The age pdf is then obtained by solving the following forward boundary value problem:

$$\frac{\partial \phi g_A}{\partial t} = -\nabla \cdot \mathbf{q} g_A + \nabla \cdot \mathbf{D} \nabla g_A + q_I \delta(t) - q_O g_A \quad \text{in } \Omega \quad (2a)$$

$$g_A(\mathbf{x}, 0) = g_A(\mathbf{x}, \infty) = 0 \quad \text{in} \quad \Omega \quad (2b)$$

$$\mathbf{J}_A(\mathbf{x}, t) \cdot \mathbf{n} = (\mathbf{q} \cdot \mathbf{n})\delta(t) \quad \text{on} \quad \Gamma_- \quad (2c)$$

$$\mathbf{J}_A(\mathbf{x}, t) \cdot \mathbf{n} = 0 \quad \text{on} \quad \Gamma_0 \quad (2d)$$

where $g_A(\mathbf{x}, t)$ is the transported age pdf [T^{-1}], $\mathbf{J}_A(\mathbf{x}, t)$ is the total age mass flux vector [LT^{-2}], \mathbf{D} is the tensor of macro-dispersion [L^2T^{-1}], $\mathbf{x} = (x, y, z)$ is the vector of cartesian coordinates [L], t is time [T], $\phi = \phi(\mathbf{x})$ is porosity or mobile water content $[-]$, \mathbf{n} is a normal outward unit vector, and $\delta(t)$ is the time-Dirac delta function [T^{-1}], which ensures a pure flux impulse on Γ_- . The source term $q_1\delta(t)$ is meant for simulating a potential internal production of water (3-D) or 2-D horizontal aquifer configurations with an areal recharge intensity q_1 . The sink term q_0g_A may result from any internal extraction of groundwater. The tensor of macro-dispersion $\mathbf{D} = \phi\mathbf{D}^* = \mathbf{D}(\mathbf{x})$ in Eq. (2a) is defined by Bear [3]:

$$\mathbf{D} = (\alpha_L - \alpha_T) \frac{\mathbf{q} \otimes \mathbf{q}}{\|\mathbf{q}\|} + \alpha_T \|\mathbf{q}\| \mathbf{I} + \phi D_m \mathbf{I} \quad (3)$$

where α_L and α_T are the longitudinal and transversal coefficients of dispersivity [L], respectively, D_m is the coefficient of molecular diffusion [L^2T^{-1}], and \mathbf{I} is the identity matrix. The total age mass flux vector $\mathbf{J}_A(\mathbf{x}, t)$ is classically defined by the sum of the convective and dispersive fluxes:

$$\mathbf{J}_A(\mathbf{x}, t) = \mathbf{q}g_A(\mathbf{x}, t) - \mathbf{D}\nabla g_A(\mathbf{x}, t) \quad (4)$$

2.3 Life expectancy probability.

The life expectancy probability distribution satisfies the adjoint backward model of Eq. (2a):

$$\frac{\partial \phi g_E}{\partial t} = \nabla \cdot \mathbf{q}g_E + \nabla \cdot \mathbf{D}\nabla g_E - q_1g_E \quad \text{in} \quad \Omega \quad (5a)$$

$$g_E(\mathbf{x}, 0) = g_E(\mathbf{x}, \infty) = 0 \quad \text{in} \quad \Omega \quad (5b)$$

$$\mathbf{J}_E(\mathbf{x}, t) \cdot \mathbf{n} = -(\mathbf{q} \cdot \mathbf{n})\delta(t) \quad \text{on} \quad \Gamma_+ \quad (5c)$$

$$-\mathbf{D}\nabla g_E(\mathbf{x}, t) \cdot \mathbf{n} = 0 \quad \text{on} \quad \Gamma_0 \quad (5d)$$

where $g_E(\mathbf{x}, t)$ is the transported life expectancy pdf, and where the total life expectancy mass flux vector $\mathbf{J}_E(\mathbf{x}, t)$ is

$$\mathbf{J}_E(\mathbf{x}, t) = -\mathbf{q}g_E(\mathbf{x}, t) - \mathbf{D}\nabla g_E(\mathbf{x}, t) \quad (6)$$

Eq. (5a) is the formal adjoint of Eq. (2a) [32,2], the so-called "backward-in-time" equation [69,73,72], also backward Kolmogorov equation [40]. Given the forward equation, the backward equation is technically obtained by reversing the sign of the flow field, and by adapting the boundary conditions [50,51,72]. On the impermeable boundary Γ_0 , a third-kind condition (Cauchy) in the forward equation becomes a second-kind condition (Neumann) in the backward equation, and vice-versa. A second-kind condition in the forward model will also become a third-kind condition in the backward model [33, p. 146]. The advection term is known to be not self-adjoint (it should be written in the form $\mathbf{q} \cdot \nabla g_E$ in Eq. (5a)) unless flow is divergence free [72]. However, the backward equation can still handle non-divergence free flow fields by means of the important sink term $-q_I g_E$ appearing in Eq. (5a). This sink term has been derived in Cornaton [13] from the vertical averaging process of the general 3-D backward ADE, and is consistent with the analysis of Neupauer and Wilson [51,52]. Recharge by internal sources (3-D or 2-D vertical) or by areal fluxes (fluid source for 2-D horizontal) is introduced by the first-order decay type term $-q_I g_E$, which is a consequence of the reversed flow field. Internal sources produce a sink of life expectancy probability, while internal sinks (term $q_O g_A$ in Eq. (2a)) do not appear in the backward model since a fluid sink may not influence the life expectancy pdf. The boundary Γ_- corresponds to the open boundary of the system (since flow is reversed) through which a free exit of life expectancy mass is expected.

The simulation of life expectancy with (5) is valid in the case of steady-state velocity fields only. Transient-state velocity fields would require another appropriate formulation of (5). For a steady-state hydraulic situation, if \mathbf{q} approaches zero in some regions of the reservoir, e.g. like in aquitards in which transport is diffusion-dominant, then (5) still holds because of the irreversible nature of dispersion. The amount of age mass diffused between an aquifer and an aquitard is proportional to concentration differences between the two media, and is the same in both the forward and backward problems. In the boundary value problems (2) and (5) the classical homogeneous Neumann boundary condition ($-\mathbf{D}\nabla g \cdot \mathbf{n} = 0$) at the outlet limit for the age problem (at the inlet limit for the life expectancy problem) is not used in order to allow a natural age/life expectancy gradient through the open boundaries. Instead, the normal projection of the dispersive flux is evaluated implicitly at the boundaries. The evaluation procedure in the framework of the finite element method is described in Cornaton et al. [14]. This kind of boundary condition, which is referred to as *Implicit Neumann condition*, enables continuity of the total mass flux at outlet. The *Implicit Neumann condition* is a generalized version of the *Free Exit condition* for parabolic equations proposed by Frind [31]. As discussed by Nauman and Buffham [48], Parker and van Genuchten [53], Kreft and Zuber [42], and Bear and Verruitj [4], total mass flux continuity at outlet permits upgradient solute movement by dispersion.

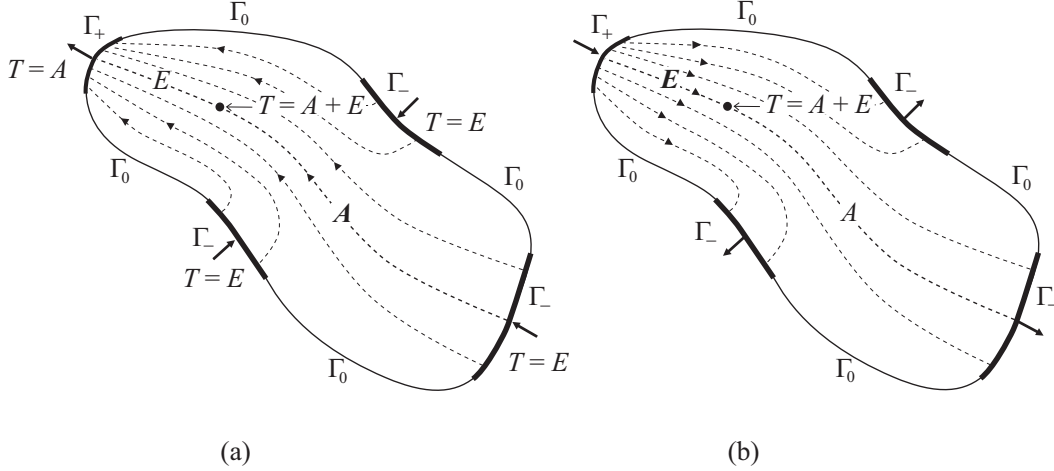


Fig. 1. Schematic illustration of a groundwater reservoir Ω , with indicated no-flow (Γ_0), inlet (Γ_-) and outlet (Γ_+) boundaries: (a) Age problem with normal flow field; (b) Life expectancy problem with reversed flow field. The arrow heads on the symbolized flowlines (dashed lines) stand for the position and direction of water molecules at a given time after their release. The black dot stands for a small water sample, to illustrate the random variable transit time (T) as the sum of the two random variables age (A) and life expectancy (E).

Eqs. (2) and (5) simulate the forward and backward transport resulting from a unit pulse input. The space-time evolution of the water molecules is described by the distributions $g_A(\mathbf{x}, t)$ and $g_E(\mathbf{x}, t)$. Both differential equations deal with conditional probabilities that characterize the statistical occurrence of water molecules as a function of age and life expectancy. Location probability is related to resident concentration [41,18,39], and describes the position \mathbf{x} of water molecules at a given time after their release in the system. On the other hand, travel time probability is related to flux concentration [41,18,39], and characterizes for a position \mathbf{x} the amount of time spent within Ω since the water molecules entered the system (in the right-hand side of Eq. (5c), age is at the flux concentration $g_A^f = \delta(t)$). Resident concentration relates to the mass of solute per unit porous volume while flux concentration is defined as the solute mass flux per unit water flux. A flux concentration is the physical representation of the mean of the microscopic fluid concentrations weighted by the associated microscopic fluid velocities [53]. The multi-dimensional relation between flux and resident concentrations can be found in Sposito and Barry [65], and is formally the projection of the total mass flux on the flow velocity direction. Accordingly, the flux concentration form of the random variable age is:

$$g_A^f = \frac{\mathbf{J}_A \cdot \mathbf{q}}{\|\mathbf{q}\|^2} = g_A + \frac{\mathbf{J}_A^d \cdot \mathbf{q}}{\|\mathbf{q}\|^2} = g_A - \frac{\mathbf{D} \nabla g_A \cdot \mathbf{q}}{\|\mathbf{q}\|^2} \quad (7)$$

with $\mathbf{J}^d = -\mathbf{D} \nabla g$ denoting the dispersive part of \mathbf{J} . By analogy, the flux

concentration form of the variable E can be defined as

$$g_E^f = -\frac{\mathbf{J}_E \cdot \mathbf{q}}{\|\mathbf{q}\|^2} = g_E - \frac{\mathbf{J}_E^d \cdot \mathbf{q}}{\|\mathbf{q}\|^2} = g_E + \frac{\mathbf{D}\nabla g_E \cdot \mathbf{q}}{\|\mathbf{q}\|^2} \quad (8)$$

The age pdf at a position \mathbf{x} in Ω characterizes the probability per unit time for the time spent since recharge, and is a flux concentration, evaluated enforcing Eq. (7). The resident concentration of age characterizes a volume-averaged age density function, which describes the density of probability of finding water molecules at the position \mathbf{x} in Ω , at time t .

2.4 Transit time probability.

In Eqs. (2a) and (5a), the dependent variables are probability density functions of continuous time random variables. The behavior of these random variables can also be described by cumulative distribution functions (cdf). Let U be one of these two variables ($U = A$ or $U = E$), with u the associated values the variable U may take at a given position \mathbf{x} of space. The cdf $G_U(\mathbf{x}, u)$ and the pdf $g_U(\mathbf{x}, u)$ of the variable U are commonly defined as

$$G_U(\mathbf{x}, u) = \text{P}[-\infty \leq U \leq u] = \int_{-\infty}^u g_U(\mathbf{x}, \tau) d\tau \quad (9)$$

with

$$g_U(\mathbf{x}, u) = \frac{\partial G_U(\mathbf{x}, u)}{\partial u} \quad , \quad G_U(\mathbf{x}, -\infty) = 0 \quad , \quad G_U(\mathbf{x}, \infty) = 1 \quad (10)$$

where P denotes the probability event on U , or number of occurrences with $U \leq u$ ratioed to the total number of occurrences, and τ is a dummy variable for integration. The probability functions property (10) together with the boundary conditions in Eqs. (2) and (5) ensure that age and life expectancy g_A and g_E are directly related to probabilities, and since concentration can be modelled by the ADE, then probability too can be modelled by the ADE. For a given position \mathbf{x} in Ω , the ages of groundwater molecules are described by the pdf g_A , which measures the density of probability of having an age t . The same molecules are also characterized by the pdf g_E , which measures the density of probability of having a life expectancy t . Introducing now the random variable transit time T , with density of probability g_T , the water molecules can be described by their intensity of probability of flowing throughout the system at a time t . The variable T is a random variable corresponding to the sum of the two random variables A and E (see Fig. 1). Hence the statistical distribution of T is the pdf of the sum of A and E , $g_T = g_{A+E}$. This problem

can be solved if the joint pdf $g_{A,E}$ of A and E , which characterizes the joint behavior of A and E , is known [5]:

$$g_T(\mathbf{x}, t) = g_{A+E}(\mathbf{x}, t) = \int_{-\infty}^{+\infty} g_{A,E}(\mathbf{x}, \tau, t - \tau) d\tau \quad (11)$$

The joint quantity $g_{A,E}(\mathbf{x}, a, e) da de$ relates to the probability that A lies in the small interval a to $a + da$, and that E lies in the small interval e to $e + de$. Assuming that A and E are stochastically independent variables (for the same spatial position, A depends on the initial point while E depends on the end point, and under a steady-state flow regime E may not be influenced by the memory of the past evolution), and since g_A and g_E are zero for negative values of their arguments, the joint pdf $g_{A,E}$ simplifies in $g_A g_E$ [5]. The probability density function g_T in Eq. (11) can then be obtained using the convolution integral:

$$g_T(\mathbf{x}, t) = \int_0^t g_A(\mathbf{x}, \tau) g_E(\mathbf{x}, t - \tau) d\tau \quad (12)$$

from which the cdf of T can be calculated enforcing Eq. (9). The fact that g_A and g_E are zero for negative values of their arguments allows applying the convolution integral from 0 to t . Since the pdfs g_A and g_E give the age and life expectancy probability of occurrence at each position \mathbf{x} in Ω , both the maximum age as well as the maximum life expectancy correspond to the maximum transit time. Consequently, the time variable t can equivalently refer to all specific values of age, life expectancy, and transit time. The convolution integral (12) states that the probability that the variable T lies in a small interval around t is proportional to the product of the probability that the variable A lies in the interval t to $t + dt$ and a factor proportional to the probability that the variable E lies in a small interval around $t - \tau$, the value of E ensuring that A and E sum to T . This product is then summed over all possible values of time t (from the minimum age to the maximum age) to yield the transit time pdf at a position \mathbf{x} in space. The derived distribution of $T = A + E$ in Eq. (12) can also be viewed as a transfer function convolution process, the input distribution being the age pdf g_A , and the signal transferring function being the life expectancy g_E .

To our point of view, Eq. (12) is an important result of the present work. The field of g_T characterizes the evolution of groundwater molecules throughout the aquifer domain by specifying the amount of time from recharge to discharge. At a given position in the reservoir, the temporal evolution of the groundwater molecules can be characterized by the three pdfs g_A , g_E and g_T . Each function contains specific information on a time of residence, the nature of which is a function of the spatial references that are chosen for evaluation. For instance, g_A is conditioned by the inlet limit Γ_- , where the variable A is nil, while g_E is conditioned by the outlet limit Γ_+ , where the variable E is nil. For the variable

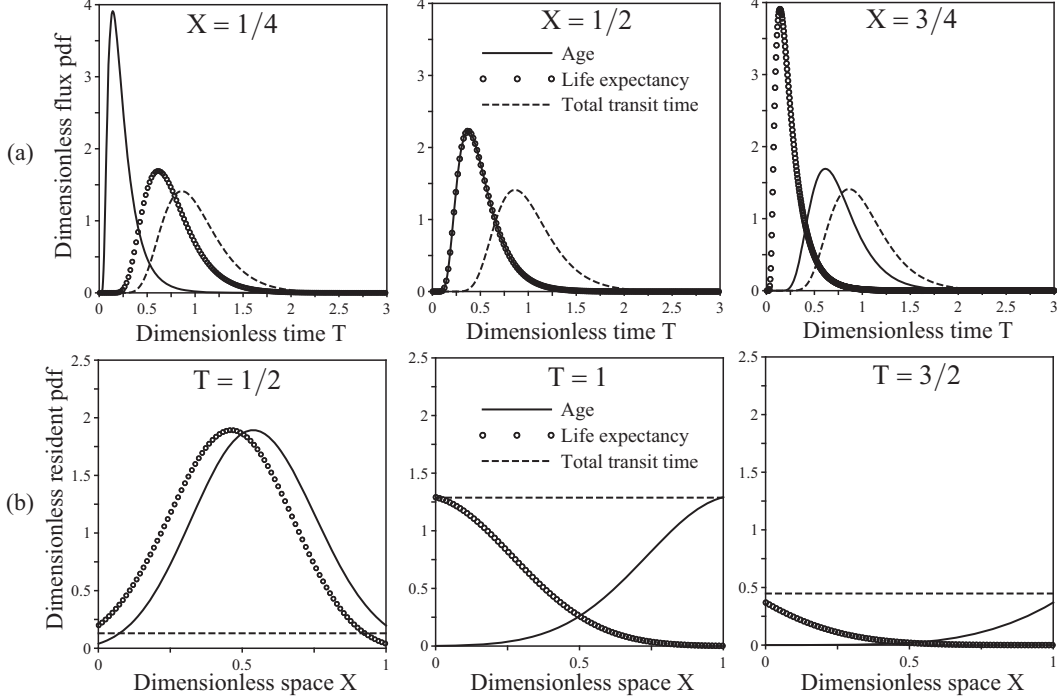


Fig. 2. Age, life expectancy and transit time dimensionless pdfs in a 1-D domain for a Péclet number $Pe = 20$: (a) Flux pdfs; (b) Resident pdfs. Time is normalized by the average turnover time $\tau_0 = L/v$, x by L , and $Pe = Lv/D$. The average age and the average life expectancy sum to the average transit time.

T , the pdf g_T is conditioned by the fact that $T = A$ at outlet, and that $T = E$ at inlet.

If g_A and g_E are resident concentrations, so is g_T . If g_A and g_E are flux concentrations, so is g_T . Applying a Laplace transform to Eqs. (7) and (8) and convoluting, the transit time resident and flux concentrations are found to be linked by the following relation:

$$\hat{g}_T^f = \hat{g}_A^f \hat{g}_E^f = \hat{g}_T - \frac{1}{\|\mathbf{q}\|^2} [\hat{g}_A \hat{\mathbf{J}}_E^d - \hat{g}_E \hat{\mathbf{J}}_A^d + \frac{(\hat{\mathbf{J}}_A^d \otimes \hat{\mathbf{J}}_E^d) \mathbf{q}}{\|\mathbf{q}\|^2}] \cdot \mathbf{q} \quad (13)$$

where $\hat{g}_U(\mathbf{x}, s)$ denotes the s -transform state of the function $g_U(\mathbf{x}, u)$, $U = A, E$ or T . Eq. (13) shows that transit time flux concentration is dependent on the transit time resident concentration, but also on the tensor product between the age and life expectancy dispersive fluxes, and on the convolution product of the age and life expectancy flux and resident concentrations. For a zero dispersion case, $g^f = g$ for the random variables A, E and T . Consider the semi-infinite 1-D domain of characteristic length L (the outlet is supposed at the position $x = L$) and uniform velocity v along the x -axis, as illustrated in Fig. 2. The age flux pdf at the position x is obtained as the solution of Eq. (2a) using the boundary condition $g_A = g_A^f = \delta(t)$ at $x = 0$, and the age resident

pdf is obtained as the solution of Eq. (2a) using the boundary condition (2c) at $x = 0$. These solutions are given in dimensionless form in Appendix A. They show the trivial fact that for a one-dimensional flow configuration, the transit time flux pdf is unique and independent on the spatial coordinate, as illustrated in Fig. 2a. For example, the age flux pdf at $X = 1/4$ in Fig. 2a is equal to the life expectancy flux pdf at $X = 3/4$, and the convolution of both distributions gives the transit time flux pdf, which equals both the age flux pdf at outlet ($X = 1$) and the life expectancy flux pdf at inlet ($X = 0$). The average age x/v and the average life expectancy $(L - x)/v$ sum to the average transit time L/v , which is independent on x in a rectilinear flow line. In a similar way, the age resident pdf at the position X equals the life expectancy resident pdf at the position $1 - X$, as shown in Fig. 2b. For a fixed value of time, the transit time resident pdf is constant. This shows that, in 1-D, the intensity of probability of finding water molecules at any position in the domain that transit at time t or less, given that t is fixed, is always identical. The transit time resident pdf gives the intensity of probability for the spatial position of water molecules, for a given value of transit time. In 1-D, this intensity of probability is uniform since the trajectory is unique. The resident age and life expectancy curves show the typical apparent discontinuity in concentration at inlet (resident pdf of A) and at outlet (resident pdf of E). These discontinuities have a drawback on the transit time resident pdf, which is not necessarily equal to the age resident pdf at outlet, and equivalently not necessarily equal to the life expectancy resident pdf at inlet. This can be attributed to dispersion effects at the boundaries. Since the Cauchy condition is homogeneous for $T = 0^+$ at inlet for the age pdf problem, and at outlet for the life expectancy pdf problem, backward movement of water molecules by dispersion (i.e. in the reserved direction of velocity) is put down by non-zero age and life expectancy resident concentrations at the boundaries, the magnitude of which is higher the higher the dispersivity. If we consider e.g. the inlet boundary, the age and life expectancy concentrations are both not nil. The convolution of both pdfs is, therefore, not equal to any of them (age pdf at outlet, life expectancy pdf at inlet) since both concentrations can have a significant value at inlet and outlet at the same time.

The spatial distribution of the transit time pdf is also ruled by a differential equation. Combining Eqs. (2a) and (5a) after a Laplace transform, the following equation can also be obtained:

$$\nabla \cdot \mathbf{q}g_T = \mathcal{L}^{-1} \{ \hat{S}_d \} \quad (14a)$$

$$\hat{S}_d = \hat{g}_E \nabla \cdot \hat{\mathbf{J}}_A^d - \hat{g}_A \nabla \cdot \hat{\mathbf{J}}_E^d \quad (14b)$$

where \mathcal{L}^{-1} denotes the inverse Laplace transform. Eq. (14a) is the transit time pdf differential equation. It is of steady-state kind, with a source term that accounts for the divergence of the age and life expectancy dispersive fluxes. For

the pure advective case in divergence-free flow fields, Eq. (14a) simplifies in $\mathbf{q} \cdot \nabla g_T(\mathbf{x}, t) = 0$. This local condition states that the flux vector and the transit time gradient have to be always perpendicular, as a requirement for keeping transit times constant along the flow paths. The resolution of Eq. (14a), which is of hyperbolic kind, is linked to technical difficulties, e.g. for the evaluation of the source term (14b) over the domain, and is not beneficial since the pdfs $g_A(\mathbf{x}, t)$ and $g_E(\mathbf{x}, t)$ must be evaluated in a preliminary step.

2.5 Mean age, mean life expectancy and mean transit time.

The average values of the probability density functions g_A , g_E and g_T are defined by their first order temporal moment, the n^{th} moment being

$$\mu_n[g_U] = \int_{-\infty}^{+\infty} u^n g_U(\mathbf{x}, u) du = (-1)^n \frac{\partial^n \hat{g}_U(\mathbf{x}, s=0)}{\partial s^n} \quad (15)$$

with $U = A, E$, or T . Applying the convolution theorem in the Laplace domain results in the transformed Eq. (12), $\hat{g}_T(\mathbf{x}, s) = \hat{g}_A(\mathbf{x}, s) \hat{g}_E(\mathbf{x}, s)$. Accounting for the pdf property $\hat{g}_U(\mathbf{x}, s=0) = 1$ and enforcing Eq. (15) for $n = 1$ and 2 yields the average transit time and its variance:

$$\langle T \rangle = \langle A \rangle + \langle E \rangle \quad (16)$$

$$\mu_2[g_T] = \mu_2[g_A] + \mu_2[g_E] + 2\langle A \rangle \langle E \rangle \quad (17)$$

$$\sigma^2[g_T] = \sigma^2[g_A] + \sigma^2[g_E] \quad (18)$$

with $\langle A \rangle = \langle A \rangle(\mathbf{x}) = \mu_1[g_A]$, $\langle E \rangle = \langle E \rangle(\mathbf{x}) = \mu_1[g_E]$ and $\langle T \rangle = \langle T \rangle(\mathbf{x}) = \mu_1[g_T]$. The average age and average life expectancy of a water sample sum up to the average transit time. Since the variables A and E are supposed to be stochastically independent, the variances σ^2 of the age and life expectancy pdfs also sum up to the variance of the transit time pdf. Using the operator in Eq. (15), Eqs. (2a) and (5a) can be transformed into their n^{th} normalized moment μ_n form. The recursive application of the operator (15) to Eqs. (2a) and (5a) yields

$$-\nabla \cdot \mathbf{q} \mu_n[g_A] + \nabla \cdot \mathbf{D} \nabla \mu_n[g_A] - q_O \mu_n[g_A] + \phi n \mu_{n-1}[g_A] = 0 \quad (19)$$

for the forward n^{th} moment ADE, and

$$\nabla \cdot \mathbf{q} \mu_n[g_E] + \nabla \cdot \mathbf{D} \nabla \mu_n[g_E] - q_I \mu_n[g_E] + \phi n \mu_{n-1}[g_E] = 0 \quad (20)$$

for the backward n^{th} moment ADE. The n^{th} moment forms of the ADEs (2a) and (5a) are only dependent on the $(n-1)^{\text{th}}$ moment μ_{n-1} . For instance, since

$\mu_0[g_A] = 1$ and $g_A(\mathbf{x}, 0) = 0$, the first moment form of Eq. (2a) (for $n = 1$) corresponds to the mean age equation as defined by Goode [35], in which the mean age is the average over a sample of water molecules of the time elapsed since recharge:

$$-\nabla \cdot \mathbf{q}\langle A \rangle + \nabla \cdot \mathbf{D}\nabla\langle A \rangle - q_O\langle A \rangle + \phi = 0 \quad \text{in } \Omega \quad (21)$$

The first moment form of Eq. (5a) gives the backward adjoint mean life expectancy equation:

$$\nabla \cdot \mathbf{q}\langle E \rangle + \nabla \cdot \mathbf{D}\nabla\langle E \rangle - q_I\langle E \rangle + \phi = 0 \quad \text{in } \Omega \quad (22)$$

Finally, the mean transit time equation is deduced by subtracting Eq. (21) and Eq. (22):

$$\mathbf{q} \cdot \nabla\langle T \rangle = \langle S_d \rangle \quad (23a)$$

$$\langle S_d \rangle = \nabla \cdot \mathbf{D}\nabla\langle A \rangle - \nabla \cdot \mathbf{D}\nabla\langle E \rangle \quad (23b)$$

where the divergence of the advection term has been developed in order to annihilate the fluid source and sink terms. The boundary value problems (2) and (5) involve that the finite moments of the age and life expectancy pdfs exist for homogeneous boundary conditions. By definition, the mean groundwater age in a steady-flow reservoir, or mean residence time, can be determined from the average of the normalized flux concentration response to a narrow flux input uniformly applied on the recharge limits, since this breakthrough curve corresponds to the water molecules residence time distribution [21,41,39]. The mean groundwater age can then be calculated by prescribing at all inflow boundaries a solute mass that is proportional to the water flux [37]. Consequently, Eqs. (21) and (22) can be solved by assigning $\langle A \rangle = 0$ on the inlet limits Γ_- , and $\langle E \rangle = 0$ on the outlet limits Γ_+ , respectively. Mean age and mean life expectancy are continuously generated during groundwater flow, since porosity acts as a source term in Eqs. (21) and (22). This source term indicates that groundwater is aging one unit per unit time, in average. The mean age and mean life expectancy equations can be easily handled by numerical codes that solve ADEs, by distributing a source term equal to porosity, and by reversing the velocity field for the case of Eq. (22). Eq. (23a) would require the boundary conditions $\langle T \rangle = \langle E \rangle$ on Γ_- , and $\langle T \rangle = \langle A \rangle$ on Γ_+ . However, mean transit time can rather be obtained by solving the Eqs. (21) and (22), and by post-processing Eq. (16). If dispersion is nil Eq. (23a) is simply $\mathbf{q} \cdot \nabla\langle T \rangle = 0$, the solution of which is comparable to the stream lines in a flow model, and associates to each line the advective transit time from inlet to outlet.

According to Parker and van Genuchten [53,54], Kreft and Zuber [41,42], and Sposito and Barry [65], temporal moments have a real physical meaning if

they are related to flux concentration functions, while spatial moments must characterize resident concentration functions. Flux and resident concentration depend themselves on the measurement technique [65,59]. An age date as deduced from isotopic measurements corresponds to an age average over the number of molecules in the water sample, and may often be close to a resident concentration. Mean age computations using Eq. (21) are, therefore, well-suited for fitting isotopic age dates.

2.6 Theoretical illustration example.

The numerical solutions presented in this work have been performed using the Laplace Transform Galerkin (LTG) finite element technique [68], which allows eliminating the time-derivative in Eqs. (2a) and (5a). The Cauchy type boundary conditions (2c) and (5c) imply that Eqs. (2a) and (5a) must be formulated according to their divergence form [23], such that a total mass flux continuity at the boundaries must be properly handled. The assembled linear system of equations is solved by the accurate ILUT-based sparse iterative solver [62] with complex arguments and GMRES [61] or BiCGSTAB [70] acceleration. The numerical inversion of the Laplace transformed functions is performed by the algorithm of Crump [15]. The quotient-difference algorithm is used to accelerate the convergence of the Fourier series [24]. This algorithm proved to be very efficient to treat inversion at the neighborhood of discontinuities or sharp fronts, and the required computational effort, which is linearly proportional to the $2n + 1$ number of discrete Laplace variables, is highly diminished with respect to other acceleration methods.

We use here the simple example of a theoretical vertical aquifer section (see Fig. 3) to illustrate age, life expectancy and transit time computations. The configuration of the flow problem corresponds to the typical case known as 'well-mixed reservoirs', that generate an exponential-like transit time distribution at outlet. This aspect will be discussed in more details in Section 4.2. The aquifer is homogeneous, and is uniformly recharged on top by a constant infiltration rate. The outlet, which could represent a trench, is simulated by means of a prescribed constant hydraulic head from the top to the bottom of the section. We solve the boundary value problems (2) and (5), as well as Eqs. (21) and (22). The model is discretized into 100'000 bilinear quadrangles of size $\Delta x = 0.5$ m and $\Delta z = 0.25$ m. Fig. 3a shows the flow field by means of a forward particle-tracking representation. Fig. 3b gives the backward particle-tracking solution, which represents the purely advective life expectancy spatial distribution. In Fig. 3c, we have plotted the solutions of Eqs. (21), (22) and (16). Mean age and mean life expectancy are in very good agreement with particle-tracking solutions. Isolines of mean age are horizontally distributed in relation to the flow configuration: velocity increases upstream to downstream

(increase of hydraulic gradient towards outlet), but also becomes more and more horizontally distributed. Travel paths to reach a same depth are longer downstream than upstream, but since velocity increases downstream, it creates a compensating effect and the corresponding travel times finally become similar, in average. Mean life expectancy gradients are mainly horizontal, and gradually increasing upstream. Mean transit time provides a good representation of the flow field; its distribution is very close to the flow lines shown in Fig. 3a. However, the mean transit time solution owns the additional information on the total time required by water molecules to travel from inlet to outlet. Finally, in Fig. 3d are given some observed pdfs (see Fig. 3a for the location of the observation points). Successive age pdfs along a horizontal profile confirm the vertical gradient of mean age shown in Fig. 3c, each age pdf at a same depth being very comparable to one other. Along a vertical profile, successive age pdfs are more and more spread in relation to the effect of longitudinal dispersion, which is bigger the longer the travel path. The behavior of the life expectancy pdfs is similar to that of age, but in the reversed direction of velocity. The transit time pdfs along a horizontal profile are very similar to each other; they are simply shifted along the axis of time. This reveals a same amount of dispersion affecting transport of water molecules along each travel path from inlet to outlet. Vertically, the functions $g_T(\mathbf{x}, t)$ show more and more dispersion with increasing depth, in relation to the vertical mixing of water molecules.

3 Generalized Reservoir Theory.

Recent studies [28,29] proposed a direct approach to calculate outlet transit time distributions by applying the reservoir theory (RT) [27,7] to the average groundwater age field, resulting from a pure advective transport solution. In the following, we show how the RT can be generalized to advective-dispersive systems by manipulating the forward and backward transport equations. We first introduce some characteristic reservoir time probability distributions. Two equivalent mathematical formulations are then proposed, in order to evaluate the discharge zone transit time pdf as a function of the reservoir internal physical properties.

3.1 Characteristic reservoir distributions.

When a specific age distribution is assigned to each elementary water volume in the reservoir, the volume of mobile water can be classified in a cumulative manner with respect to the age occurrence in the reservoir. Let $M_A(t)$ be the cumulated amount of water molecules in the reservoir with an age inferior

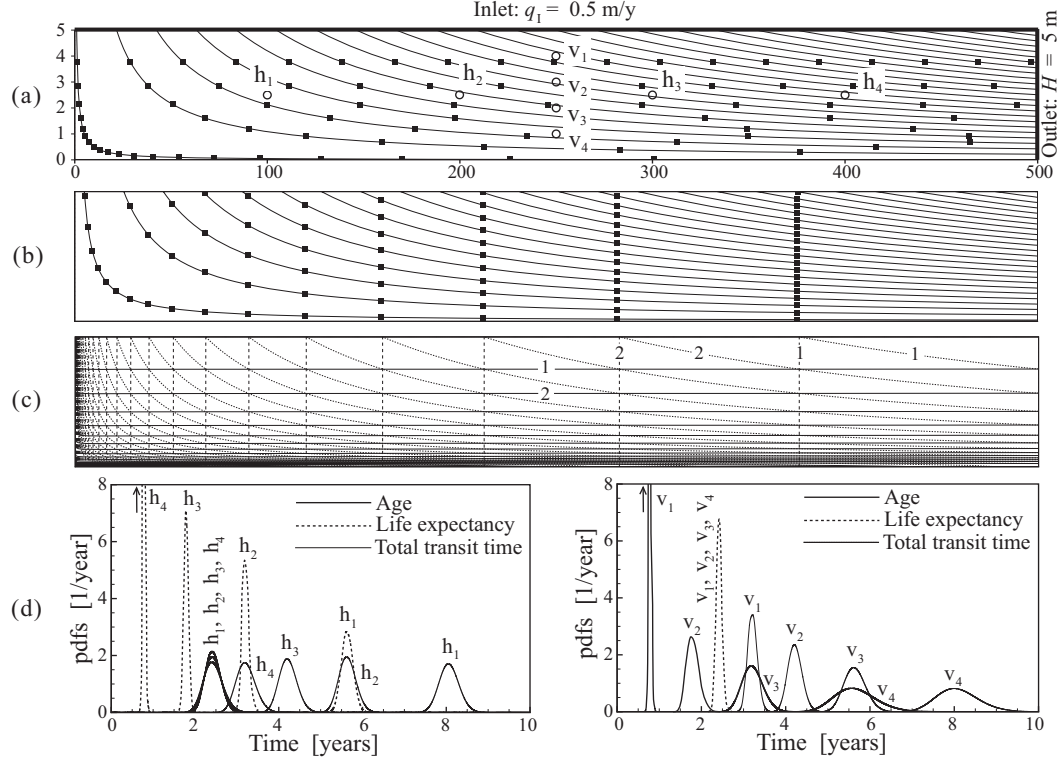


Fig. 3. Age, life expectancy and transit time computations in a 2-D vertical theoretical aquifer. (a) Geometry, boundary conditions and flow field representation by forward particle-tracking with marker-isochrones each 1 year; (b) Backward particle-tracking with marker-isochrones each 1 year; (c) Spatial distribution of mean age (solid lines), mean life expectancy (dashed lines) and mean transit time (dotted lines) with 1 year of time-increment; (d) Age, life expectancy and transit time pdfs at some observations points. Parameters: $K = 10^{-4}$ m/s, $\phi = 0.35$, $\alpha_L = 0.1$ m, $\alpha_T = 0.001$ m, $D_m = 0$.

or equal to a particular value t , and $m_A(t)$ be the corresponding probability function, or reservoir internal age cdf. The function $m_A(t)$ is the porous volume normalized function $M_A(t)$, which is evaluated by integrating over Ω the probability of finding water molecules with an age t or less, assuming that each molecule has entered the system on Γ_- :

$$m_A(t) = \frac{M_A(t)}{M_0} = \frac{1}{M_0} \int_{\Omega} \phi G_A(\mathbf{x}, t) d\Omega = \frac{1}{M_0} \int_{\Omega} \phi \left(\int_0^t g_A(\mathbf{x}, \tau) d\tau \right) d\Omega \quad (24)$$

with M_0 being the total amount of mobile water (aquifer porous volume). The function $m_A(t)$ cumulates the probability of finding water molecules which have travelled until a position \mathbf{x} before time t . The function $M_A(t)$ is zero at origin and tends towards the total porous volume M_0 at infinity. The internal age frequency distribution function $\psi_A(t)$ is the pdf associated to $m_A(t)$, and

from Eq. (10) it follows

$$\psi_A(t) = \frac{\partial m_A(t)}{\partial t} = \frac{1}{M_0} \int_{\Omega} \phi g_A(\mathbf{x}, t) d\Omega \quad (25)$$

Note that Eq. (25) corresponds to the zeroth spatial moment of the age pdf, which is equivalent to the age mass [59]. The function $\psi_A(t)$ gives the probability density of finding elements in Ω that have reached the age t , and $\psi_A(t)dt$ is the probability that A lies in the interval $[t, t+dt]$. Thus, the quantity $M_0\psi_A(t)$ represents the number of elements per unit time (or flow rate fraction) that are in the interval $[t, t+dt]$, and is equivalent to the zeroth spatial moment of the age pdf $g_A(\mathbf{x}, t)$. We similarly define the internal life expectancy cdf $m_E(t)$ and pdf $\psi_E(t)$:

$$m_E(t) = \frac{M_E(t)}{M_0} = \frac{1}{M_0} \int_{\Omega} \phi G_E(\mathbf{x}, t) d\Omega = \frac{1}{M_0} \int_{\Omega} \phi \left(\int_0^t g_E(\mathbf{x}, \tau) d\tau \right) d\Omega \quad (26)$$

$$\psi_E(t) = \frac{\partial m_E(t)}{\partial t} = \frac{1}{M_0} \int_{\Omega} \phi g_E(\mathbf{x}, t) d\Omega \quad (27)$$

The function $m_E(t)$ cumulates the probability that a water molecule in the reservoir will reach the outlet before time t .

We finally consider the internal distribution of the groundwater molecules transit time pdf g_T as deduced from the convolution integral in Eq. (12), to introduce the functions $m_T(t)$ and $\Psi(t)$ as the internal transit time cdf and pdf, respectively:

$$m_T(t) = \frac{M_T(t)}{M_0} = \frac{1}{M_0} \int_{\Omega} \phi G_T(\mathbf{x}, t) d\Omega = \frac{1}{M_0} \int_{\Omega} \phi \left(\int_0^t g_T(\mathbf{x}, \tau) d\tau \right) d\Omega \quad (28)$$

$$\Psi(t) = \frac{\partial m_T(t)}{\partial t} = \frac{1}{M_0} \int_{\Omega} \phi g_T(\mathbf{x}, t) d\Omega \quad (29)$$

The function $M_T(t)$ corresponds to the mass of mobile water in the reservoir having a transit time inferior or equal to t . The function $\Psi(t)$ characterizes the probability density of finding water molecules within the reservoir that have a transit time inferior or equal to t , and the quantity $M_0\Psi(t)dt$ gives the amount of water molecules that travel through Ω within the time interval $[t, t+dt]$.

3.2 The transit time pdf of discharge and recharge zones.

A reservoir discharge zone is a particular portion of finite size, which intercepts the groundwater molecules that contribute to the outflow rate. These

water molecules have contrasted arrival times that converging water fluxes mix together before flowing out. At a given position on a discharge boundary, the transit time pdf is the age pdf. To characterize the contribution of each age flux event on an outflow boundary in terms of transit time probability, it is convenient to average the age probability fluxes on Γ_+ . Under steady-flow regime, the representative transit time distribution $\varphi_A(t)$ of the reservoir outlet zone can be defined as a flux averaged concentration [59], i.e. $\varphi_A(t)$ is evaluated as the flow rate-normalized sum on Γ_+ of the total age mass flux response function \mathbf{J}_A resulting from a unit flux impulse on Γ_- :

$$\varphi_A(t) = \frac{1}{F_0} \int_{\Gamma_+} \mathbf{J}_A \cdot \mathbf{n} d\Gamma = \frac{1}{F_0} \int_{\Gamma_+} [\mathbf{q}g_A - \mathbf{D}\nabla g_A] \cdot \mathbf{n} d\Gamma \quad (30)$$

where \mathbf{n} is a normal unit vector pointing outward the boundary, and where F_0 represents the total discharge flow rate throughout the bounded domain, which at steady-state is evaluated by:

$$F_0 = \int_{\Gamma_+} \mathbf{q}(\mathbf{x}) \cdot \mathbf{n} d\Gamma = \int_{\Gamma_-} \mathbf{q}(\mathbf{x}) \cdot \mathbf{n} d\Gamma \quad (31)$$

Note that for the sake of simplicity, internal sources and sinks are neglected, $q_I = q_O = 0$. While flux concentrations are defined with respect to a control plane orthogonal to the velocity vector direction, the outlet transit time probability function in Eq. (30) is defined by the projection of the total age flux on the arbitrary-shaped boundary Γ_+ . Inserting Eq. (7) into Eq. (30) produces the equivalent relation:

$$\varphi_A(t) = \frac{1}{F_0} \int_{\Gamma_+} \left[\mathbf{q}g_A^f - \left(\mathbf{I} - \frac{\mathbf{q} \otimes \mathbf{q}}{\|\mathbf{q}\|^2} \right) \mathbf{D}\nabla g_A \right] \cdot \mathbf{n} d\Gamma \quad (32)$$

With Eq. (32), one can see that, if the velocity vector \mathbf{q} points in the direction of the outward normal unit vector \mathbf{n} , then the dispersive term inside the brackets vanishes, and the pdf $\varphi_A(t)$ is equal to the total steady flow rate-normalized sum of the flux-weighted age flux concentration pdfs on the outlet limit. This is always the case in one-dimension. The cross product term in Eq. (32) reveals also that since the outflow limit is of arbitrary shape, then when velocity does not point in the direction of \mathbf{n} a dispersive correction term is required. This is related to the fact that flux concentrations are defined with respect to a control plane which is orthogonal to the velocity direction.

The discharge flow rate can also be described as a cumulative function of the transit time values. We introduce the function $f_A(t)$ as the transit time cdf of the reservoir outlet, i.e. $f_A(t)$ is the probability that the molecules flow out with a transit time t or less, such that it corresponds to the normalized

cumulated outflow function $F_A(t)$:

$$f_A(t) = \frac{F_A(t)}{F_0} = \int_0^t \varphi_A(\tau) d\tau \quad (33)$$

Note that the function $f_A(t)$ can also be viewed as the integral on Γ_+ of the total mass flux deduced from the resident concentration solutions of the ADE (2a) for a unit step-input of mass flux on Γ_- . By analogy, the life expectancy pdf and cdf of the reservoir inlet Γ_- can similarly be defined by

$$\begin{aligned} \varphi_E(t) &= \frac{1}{F_0} \int_{\Gamma_-} \mathbf{J}_E \cdot \mathbf{n} d\Gamma = -\frac{1}{F_0} \int_{\Gamma_-} [\mathbf{q}g_E + \mathbf{D}\nabla g_E] \cdot \mathbf{n} d\Gamma \\ &= -\frac{1}{F_0} \int_{\Gamma_-} \left[\mathbf{q}g_E^f + \left(\mathbf{I} - \frac{\mathbf{q} \otimes \mathbf{q}}{\|\mathbf{q}\|^2} \right) \mathbf{D}\nabla g_E \right] \cdot \mathbf{n} d\Gamma \end{aligned} \quad (34)$$

$$f_E(t) = \frac{F_E(t)}{F_0} = \int_0^t \varphi_E(\tau) d\tau \quad (35)$$

Eq. (13) indicates that the transit time flux pdf equals both the life expectancy flux pdf at inlet, and the age flux pdf at outlet. As a matter of fact, assuming neither addition nor subtraction of mass during transport, steady-flow conditions and stationary state, then, theoretically, every probability flux \mathbf{J}_A on Γ_+ has an identical counterpart \mathbf{J}_E on Γ_- and vice-versa. Therefore, Eqs. (30), (32) and (34) relate to the same and unique function, $\varphi(t) = \varphi_A(t) = \varphi_E(t)$, and thus $f(t) = f_A(t) = f_E(t)$. In fact, each element added in the reservoir at the inlet must exit at some position \mathbf{x}_o of the outlet sooner or later. Each element added at the position \mathbf{x}_o at the outlet must travel the same distance upstream, and thus spend the same time-span within the reservoir, backward in time, before reaching a position somewhere at the inlet limit.

At the reservoir outlet, the arrival times g_A are distributed along the discharge boundary, implying mixing and superposition of the information carried by each breakthrough curve. Moreover, within the reservoir mixing processes can also be important, and the true minimum and maximum ages can be diluted. To characterize an outlet representative transit time distribution, we must ensure that the minimum and the maximum ages are captured. Technical problems can often occur when solving Eq. (30) or Eq. (34), because mass flux line/surface integration is required. If the outlet is of small size, then the capture of calculated breakthrough curves, or the identification of particle arrivals, reveals to be ill-posed, mainly because of the loss of information due to the mixing of converging fluxes. Hence, numerical methods will generally require a high level of refinement in the neighborhood of these integration limits, which rapidly becomes a computational limiting factor. Because the transit time pdf $\varphi(t)$ on the inlet limit is identical on the outlet limit, discretization

methods imply that the number of observation nodes should be the same at the inlet and at the outlet, in order to be able to recover the same breakthrough curves. In other words, the temporal resolution of the curve, when a counting of the individual arrival times is performed, is a direct function of the spatial refinement in the vicinity of exit zones. The same restriction affects other simulation methods, such as the random-walk procedure.

In the following, we propose an alternative approach that is relaxed from the above-mentioned practical problems. Eqs. (2) and (5) are considered to simulate the age and life expectancy probability distributions in the reservoir Ω . Integrating Eq. (2a) over Ω , and making use of the divergence theorem ($\int_{\Omega} \nabla \cdot \mathbf{F} d\Omega = \int_{\Gamma} \mathbf{F} \cdot \mathbf{n} d\Gamma$) results in

$$\int_{\Gamma_+} [\mathbf{q}g_A - \mathbf{D}\nabla g_A] \cdot \mathbf{n} d\Gamma + \frac{\partial}{\partial t} \int_{\Omega} \phi g_A d\Omega = - \int_{\Gamma_-} [\mathbf{q}g_A - \mathbf{D}\nabla g_A] \cdot \mathbf{n} d\Gamma \quad (36)$$

Normalizing Eq. (36) by the steady flow rate F_0 and accounting for Eq. (25) and (30), Eq. (36) can be turned into the following form:

$$\varphi_A(t) + \tau_0 \frac{\partial \psi_A(t)}{\partial t} = - \frac{1}{F_0} \int_{\Gamma_-} [\mathbf{q}g_A - \mathbf{D}\nabla g_A] \cdot \mathbf{n} d\Gamma \quad (37)$$

with the quantity τ_0 being the turnover time commonly defined at steady-state as the ratio of porous volume to flow rate:

$$\tau_0 = \frac{M_0}{F_0} \quad (38)$$

Similarly, the integration of the ADE (5a) has the form

$$- \int_{\Gamma_+} [\mathbf{q}g_E + \mathbf{D}\nabla g_E] \cdot \mathbf{n} d\Gamma + \frac{\partial}{\partial t} \int_{\Omega} \phi g_E d\Omega = \int_{\Gamma_-} [\mathbf{q}g_E - \mathbf{D}\nabla g_E] \cdot \mathbf{n} d\Gamma \quad (39)$$

Normalizing Eq. (39) by F_0 and accounting for Eq. (27) and (34) yields

$$\varphi_E(t) + \tau_0 \frac{\partial \psi_E(t)}{\partial t} = \frac{1}{F_0} \int_{\Gamma_-} [\mathbf{q}g_E - \mathbf{D}\nabla g_E] \cdot \mathbf{n} d\Gamma \quad (40)$$

The boundary integrals in the right-hand sides of Eqs. (37) and (40) can be simplified by accounting for the boundary conditions (2c) and (5c). For instance, inserting the boundary condition (2c) into Eq. (37) reduces the boundary integral to $-F_0\delta(t)$, and inserting the boundary condition (5c) into

Eq. (40) reduces the boundary integral to $F_0\delta(t)$, and Eqs. (37) and (40) become:

$$\varphi_A(t) + \tau_0 \frac{\partial \psi_A(t)}{\partial t} = \delta(t) \quad (41a)$$

$$\varphi_E(t) + \tau_0 \frac{\partial \psi_E(t)}{\partial t} = \delta(t) \quad (41b)$$

With Eq. (41a) we have recovered the RT formulation of Eriksson [27], in which the outlet zone transit time pdf $\varphi_A(t)$ is proportional to the first derivative of the internal age pdf $\psi_A(t)$, thus characterizing the probability for the water molecules of being removed from Ω per unit time. Eq. (41b) is an equivalent formulation which relates the recharge boundary life expectancy distribution to the internal life expectancy distribution. Since the functions $\varphi_A(t)$ and $\varphi_E(t)$ are equal, it follows from Eqs. (41a) and (41b) that $\psi_A(t) = \psi_E(t)$, which allows writing the following general RT formulation:

$$\varphi(t) + \tau_0 \frac{\partial \psi(t)}{\partial t} = \delta(t) \quad (42)$$

Eq. (42) generalizes the RT to advective-dispersive solute transport processes, and is valid for both age and life expectancy. If dispersion is set to zero, the function $\psi(t)$ can be evaluated by integration of the field $g_A(\mathbf{x}, t) = \delta(t - \langle A \rangle(\mathbf{x}))$ as proposed by Etcheverry and Perrochet [28,29]. Similarly, the function $\psi(t)$ can be evaluated by integration of the field $g_E(\mathbf{x}, t) = \delta(t - \langle E \rangle(\mathbf{x}))$. Since $\psi(t) = \psi_A(t) = \psi_E(t)$, it follows from Eq. (9) that $M(t) = M_A(t) = M_E(t)$. This points out the importance in allowing age and life expectancy dispersive fluxes crossing naturally the outlet and inlet boundary portions, because the use of the homogeneous Neumann condition on Γ_+ and may lead to different results for $\varphi(t)$ if contrasted boundary configurations and flow conditions exist. The third-kind boundary conditions (2c) and (5c) are the most meaningful conditions for solving the age and life expectancy problems. They ensure a pure total flux pulse input entering the system at inlet for the age problem, and at outlet for the life expectancy problem. These conditions become homogeneous for $t > 0$ (zero flux), and do not allow backward mass losses by dispersion. This would not be the case when using a Dirichlet type condition, which may lead to incorrect solute mass balances. For the one-dimensional case, the use of the Dirichlet condition permits the simulation of the age and life expectancy pdfs, but directly for flux concentration pdfs (see Appendix A).

The fundamental relation between the outlet transit time cdf $f(t)$ and the internal age pdf $\psi(t)$ given by the RT is obtained after integration of Eq. (42):

$$F_0 - F(t) = M_0\psi(t) = \frac{\partial M(t)}{\partial t} \quad (43)$$

or

$$f(t) + \tau_0 \psi(t) = 1 \quad (44)$$

Eq. (43) indicates that the outflow of water molecules that leave the system through Γ_+ with an age older than t is balanced by the number of elements per unit time within Ω that reach the age t , i.e. in the interval $[t, t + dt]$. The corresponding volume of groundwater reaching the age t in Ω is $M_0 \psi(t) dt$. In other words, the flow rate fraction of age t or less at the outlet is a function of the spatial occurrence in the reservoir of water molecules of age t or less. Since the function $f(t)$ is zero at the origin, it follows that the value of $\psi(t)$ at origin is the turnover rate σ_0 ($\psi(0) = \sigma_0 = 1/\tau_0$), independently of the level of dispersion. Since $f(t)$ is a cumulative function, then $\psi(t)$ must be monotonically decreasing and $M(t)$ must be an increasing function with monotonically decreasing increments [27]. The pdf $\psi(t)$ is constant from zero to the minimum age t_{\min} at outlet, with $\psi(0, \dots, t_{\min}) = \sigma_0$, which throws light on the fact that the probability per unit time of finding elements in Ω that have reached the age $t \leq t_{\min}$ is certain. From Eq. (43) it follows that $M(t)$ has a constant derivative equal to $M_0 \psi(0) = F_0$ until the minimum age t_{\min} is reached at outlet. Note that the same considerations can be made for $f(t) = f_E(t)$, $\psi(t) = \psi_E(t)$ and $M(t) = M_E(t)$.

Fig. 4 illustrates in 1-D the outlet (or inlet) transit time pdf, the internal age (or life expectancy) pdf, and the internal transit time pdf resulting from the analytical resolution of Eqs. (25), (29) and (42) (see Appendix A). Under pure convective transport conditions (dashed lines in Fig. 4), the function $\varphi(t)$ equals the piston-flow transit time pdf $\delta(t - \tau_0)$, and the function $\psi(t)$ is the Heaviside function $H(\tau_0 - t)/\tau_0$, such that $\psi(t) = \psi(0) = 1/\tau_0$ until $t_{\min} = \tau_0$, and $\psi(t) = 0$ after t_{\min} . The first temporal moment of the pdf $\varphi(t)$ (average transit time at outlet τ_t) is dispersion-independent, and equals the turnover time τ_0 . The average internal transit time τ_{it} and the average internal age τ_i (first temporal moments of $\Psi(t)$ and $\psi(t)$) are dispersion dependent. Increasing longitudinal dispersion (low Péclet numbers) generates short arrival times and tailing effects (see the variances of the pdfs in Appendix A), and thus old arrival times at the outlet as well as old ages within the domain, which are visible on the three functions $\varphi(t)$, $\psi(t)$ and $\Psi(t)$ for a range of Péclet numbers. The function $\psi(t)$ is constant from 0 until the minimum age at outlet. Since the Cauchy type condition prevents backward losses by dispersion at $x = 0$, the value of $\psi(t)$ at the origin is always $1/\tau_0$ for any Péclet number (Fig. 4b). From the spatial organization of age or life expectancy occurrence it is possible to predict the transit time distribution of a reservoir outlet (or equivalently the life expectancy distribution of a reservoir inlet), without the need of 'counting' the arrivals of the water molecules at a boundary of finite size. Thus, the pdf $\varphi(t)$ defined in Eqs. (30) or (34) as a pure boundary property becomes a property of the reservoir internal structure and hydro-dispersive characteristics. The information that can be lost when $\varphi(t)$

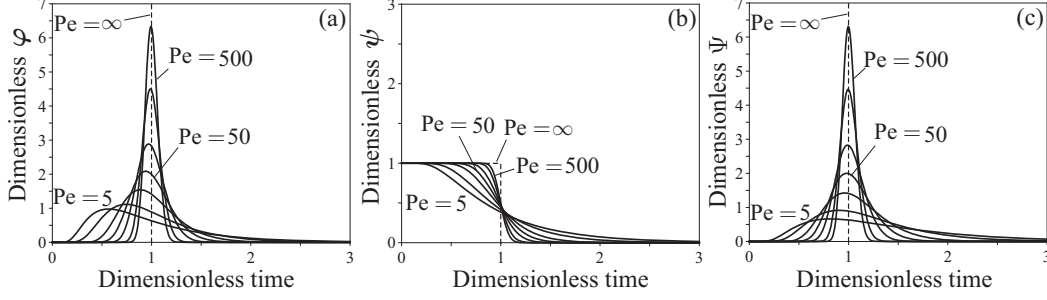


Fig. 4. Reservoir theory pdfs for a 1-D semi-infinite flow domain, as a function of the Péclet number for $Pe = 5, 10, 25, 50, 100, 250$ and 500 . (a) Outlet transit time pdf; (b) Internal age (or life expectancy) pdf; (c) Internal transit time pdf. Time is normalized by the average turnover time $\tau_0 = L/v$, x by a characteristic length L , and $Pe = Lv/D$.

is directly evaluated at the reservoir exit zone (or inlet zone) is recovered with Eq. (42). A far more accurate evaluation of $\varphi(t)$ is thus achieved, for which the main operation (domain integrals (25) and (27)) is not time-consuming and can easily be implemented for one-, two- and three-dimensional systems. A convenient way to compute Eq. (42) is to work in the Laplace space, since it allows handling all time-dependent quantities in a quasi-analytical way.

3.3 Temporal moments of the reservoir theory probability density functions.

A direct consequence of the RT is that the expected value of the mean residence time, i.e. the average transit time τ_t at outlet or inlet, equals the reservoir mean turnover time τ_0 . This property can be found by calculating the first temporal moment of the transit time pdf $\varphi(t)$, and by making use of Eq. (44):

$$\tau_t = \int_0^{+\infty} t\varphi(t)dt = \int_0^{+\infty} [1 - f(t)]dt = \tau_0 \int_0^{+\infty} \psi(t)dt = \tau_0 = \frac{M_0}{F_0} \quad (45)$$

where use has been made of the pdf property in Eq. (10). Since the reservoir is considered under steady flow conditions, internal average time characteristics can be defined. The temporal moments of the global functions $\psi(t)$ and $\Psi(t)$ have physical significance since resident concentration has been integrated in space. The mean internal age τ_{ia} and the mean internal life expectancy τ_{ie} are deduced from the first temporal moment of the function $\psi(t)$. Integrating by parts and making use of the relation (42) results in:

$$\begin{aligned} \tau_i &= \int_0^{+\infty} t\psi(t)dt = \left. \frac{t^2\psi(t)}{2} \right|_0^{+\infty} - \frac{1}{2} \int_0^{+\infty} t^2 \frac{\partial\psi(t)}{\partial t} dt = \frac{1}{2\tau_0} \int_0^{+\infty} t^2\varphi(t)dt \\ &= \frac{\mu_2[\varphi]}{2\tau_0} = \frac{\tau_0}{2} \left(1 + \frac{\sigma^2[\varphi]}{\tau_0^2} \right) \end{aligned} \quad (46)$$

Since $\psi_A(t) = \psi_E(t) = \psi(t)$, we have set $\tau_{ia} = \tau_{ie} = \tau_i$. Using Eq. (16), the average internal transit time τ_{it} is deduced from the first temporal moment of the function $\Psi(t)$, and is found to be equal to twice the value of τ_i :

$$\begin{aligned}\tau_{it} &= \int_0^{+\infty} t\Psi(t)dt = \frac{1}{M_0} \int_{\Omega} \phi \int_0^{+\infty} t g_T(\mathbf{x}, t) dt d\Omega = \frac{1}{M_0} \int_{\Omega} \phi \langle T \rangle d\Omega \\ &= \frac{1}{M_0} \int_{\Omega} \phi \langle A \rangle d\Omega + \frac{1}{M_0} \int_{\Omega} \phi \langle E \rangle d\Omega = 2\tau_i\end{aligned}\quad (47)$$

Using Eq. (42), integrating by parts and inserting Eq. (46), the second temporal moment and the variance of the distribution $\varphi(t)$ reveal themselves as being functions of τ_0 and τ_i (or τ_{it}) only:

$$\mu_2[\varphi] = \int_0^{+\infty} t^2 \varphi(t) dt = 2\tau_0 \tau_i = \tau_0 \tau_{it} \quad (48a)$$

$$\sigma^2[\varphi] = \tau_0(2\tau_i - \tau_0) = \tau_0(\tau_{it} - \tau_0) \quad (48b)$$

Finally note that by using the same technique than in Eq. (46), one can show that the second moment of $\psi(t)$ is a function of the third moment of $\varphi(t)$, $\mu_3[\varphi] = 3\tau_0\mu_2[\psi]$.

3.4 Accuracy of the RT approach.

The accuracy of the RT method compared to a classical evaluation of the transit time pdf $\varphi(t)$ at the outlet limit is illustrated in Fig. 5, using a four-layered vertical aquifer. The outlet zone is of very small size (Fig. 5a), which forces the information on age to be highly mixed. As attested by Fig. 5b, the individual age pdfs at outlet can be of very different shape. The differences between the two evaluation methods are very important. The flux-weighted sum of the age mass fluxes monitored at the outlet nodes suffers from a loss of information induced by the mixing of converging fluxes at the outlet surroundings. With the RT, this information is recovered, since we ensure that each contribution to the outflow rate is accounted for. According to Eq. (45), the average residence time τ_t must equal the turnover time τ_0 ; it is clear with this example that this property is not satisfied by straight application of Eq. (30), while the RT provides a very accurate solution (Fig. 5c).

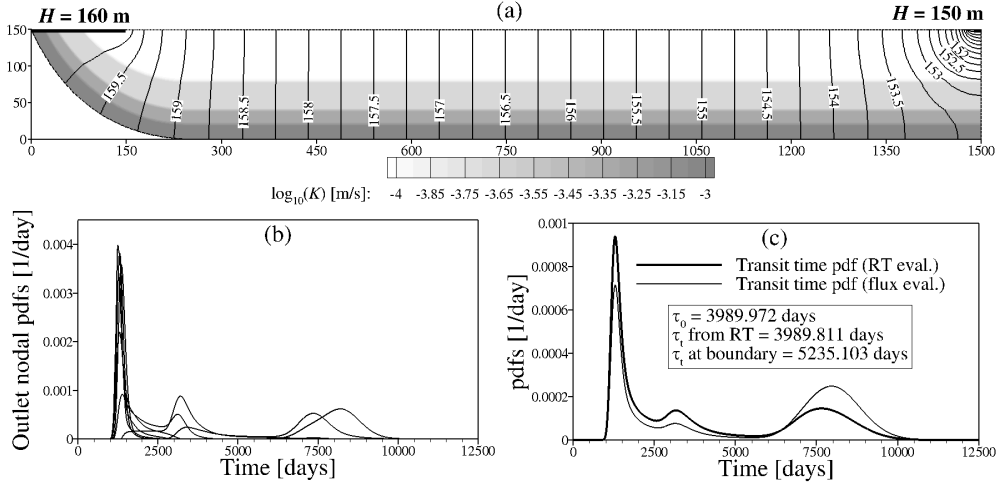


Fig. 5. Theoretical four-layered aquifer illustrating the accuracy of the RT compared to the classical direct evaluation at the outlet of the function $\varphi(t)$. (a) Model geometry, boundary conditions and head solution in meters; (b) Age pdfs monitored at outlet, from which a flux-weighted average evaluation of the transit time pdf is performed; (c) Outlet transit time pdf evaluated at outlet and using the RT. Transport parameters: $\alpha_L = 2.5$ m, $\alpha_T = 0.01\alpha_L$, $D_m = 0$.

4 Direct evaluation of aquifer water volumes versus age, life expectancy and transit time.

The specific groundwater volumes related to a given range of ages or residence times are important quantities to consider when addressing aquifer management strategies. Assessing the long-term evolution of groundwater chemistry, or defining corrective measures aiming at restoring groundwater quality after a contamination event, indeed requires appropriate age and volume-related information. In this section, we complete the framework of the RT by analyzing the transit time cdf $f(t)$ to show how complex aquifer porous volumes can directly be quantified as a function of age, life expectancy, and transit time.

4.1 Characteristic groundwater volume functions.

Provided the residence time distribution $\varphi(t)$ and the total discharge F_0 are known, the characterization of internal groundwater volumes can be done in a relatively straightforward manner by a simple analysis of the function $F(t)$ as defined in Eq. (33), $F(t) = F_0 \int_0^t \varphi(u) du$. In Fig. 6, the theoretical shape of the cumulated outflow function $F(t)$ (or cumulated inflow function) is represented. The areas v_A , v_T , and v_0 in Fig. 6a characterize different groundwater volumes that can be defined as functions of time t (Fig. 6b). The area $v_A(t)$ represents the total groundwater volume V in Ω of age inferior or equal to t but that will experience a transit time superior to t :

$$v_A(t) = V_\Omega \{A \leq t \text{ and } T > t\} = t[F_0 - F(t)] = M_0 t \psi(t) \quad (49)$$

In Eq. (49), the pdf $\psi(t)$ is expressed given the relationship (43) between $\psi(t)$ and $F(t)$. When the minimum transit time t_{\min} is not nil, the function $v_A(t)$ contains the volume of age inferior or equal to time t_{\min} , which is the area $v_{A1}(t) = t_{\min}(F_0 - F(t))$, and the volume of age inferior or equal to t and superior to time t_{\min} , which is the area $v_{A2}(t) = (t - t_{\min})(F_0 - F(t))$. The area $v_T = v_T(t)$ is the volume of groundwater that flows through Ω with a transit time t or less:

$$v_T(t) = V_\Omega \{T \leq t\} = tF(t) - v_0(t) \quad (50)$$

with the area $v_0(t)$ being the amount of exfiltrated water having travelled from inlet to outlet during an observation time period t ,

$$v_0(t) = V_{\Gamma_+} \{A \leq t\} = \int_0^t F(u) du = tF_0 - M(t) , \quad (51)$$

and where use has been made of Eqs. (25) and (43) to express the function $M(t)$. The quantity $tF(t)$ in Eq. (50) is the total amount of groundwater water in Ω that reaches the age t or less on Γ_+ , plus the volume flowing out with an age t or less. The amount of groundwater water $v_T(t)$ is nil until the minimum transit time t_{\min} , and reaches the total porous volume at the maximum transit time t_{\max} . The function $v_T(t)$ contains the volume of age inferior or equal to time t_{\min} , which is the area $v_{T1}(t) = t_{\min}F(t)$ in Fig. 6a, and the volume of age superior to time t_{\min} , which is the area $v_{T2}(t) = (t - t_{\min})F(t) - v_0(t)$ in Fig. 6a. Note also that the total amount of groundwater of age t_{\min} or less is given by the sum $v_{A1} + v_{T1} = t_{\min}F_0$.

Since the amount of groundwater $v_T(t)$ is the internal volume that will leave the reservoir up to time t , it equals the internal transit time cumulative distribution function, $v_T(t) = M_T(t)$, and it represents a part of the function $M(t)$. The complementary part is the amount of groundwater water of age t or less and of transit time superior to t , namely the function $v_A(t)$ defined in Eq. (49):

$$M(t) = V_\Omega \{A \leq t\} = v_A(t) + v_T(t) \quad (52)$$

With Eq. (52), one can express $v_A(t)$ as the difference between two increasing functions that both tend to the porous volume M_0 at infinity. The function $v_A(t)$ is thus zero at the origin and at infinity. Since $v_T(t)$ is zero until the minimum transit time t_{\min} , $v_A(t)$ must equal $M(t)$ between 0 and t_{\min} . During this time-span, which can be taken as the signature of badly recharged and/or advection-dominated systems for significant values of t_{\min} , these two functions have a constant derivative (see Fig. 6b) equal to the steady flow rate $F_0 = M_0\psi(0)$. The behavior of this function (number of peaks, compared durations of increasing and decreasing parts) is instructive as to the volumetric proportions of groundwater remaining a long time in the system, or flowing quickly to the outlet. The time after which the function $v_A(t)$ starts to decrease gives information on the importance of the water volumes in the aquifer with long or short transit times. If this time is relatively young, then the aquifer may present a good turn-over property, and vice-versa.

Differentiating Eq. (52) with respect to time, and accounting for Eqs. (25), (29) and (42), yields

$$\varphi(t) = \frac{\tau_0}{t} \Psi(t) \quad (53)$$

This fundamental relation includes all the features of the RT in the most compact form. Compared to the standard rule (42), Eq. (53) is a great improvement. It is simpler and may provide the transit time distribution $\varphi(t)$ with much higher resolution and accuracy, in relation with the fact that no differentiation between $\varphi(t)$ and $\Psi(t)$ is required.

Note that if $F(t)$ characterizes the inlet cumulated inflow rate, i.e. $F(t) = F_0 f_E(t)$, then each aquifer porous volume defined above as a function of age

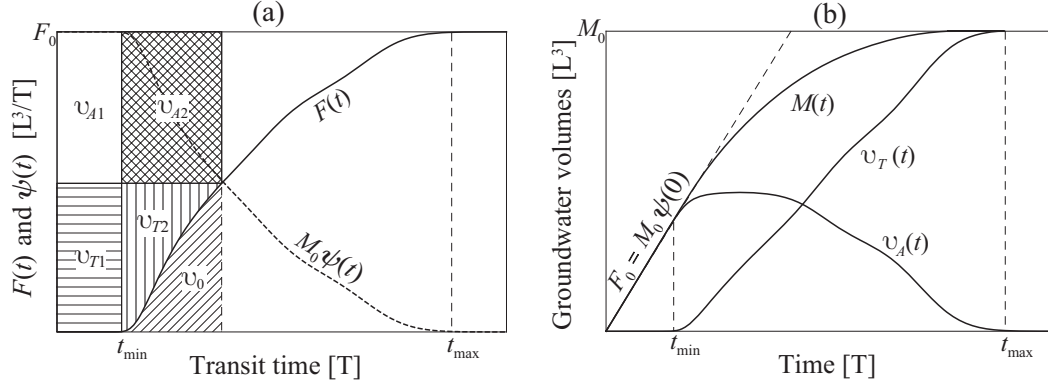


Fig. 6. Theoretical cumulated outflow function, internal age pdf (scaled by the porous volume) and internal groundwater volume functions: (a) Cumulated outflow function $F(t)$, with the indicated areas v_A , v_T and v_0 representing characteristic internal groundwater volumes relative to a value of time; (b) Aquifer porous volumes $M(t)$, $v_A(t)$ and $v_T(t)$ as a function of age and transit time.

becomes a function of life expectancy. By analyzing the system outlet transit time cdf, the quantification of complex groundwater volumes with respect to age, life expectancy, and transit time, is straightforward, and provides important practical system insights. An obvious application is the groundwater resources protection and vulnerability assessments. The underground storage of toxic wastes also requires the knowledge of groundwater volumes that are potentially subject to contamination, and assumptions on the time spent by these volumes within the reservoir until they reach an outlet area.

4.2 Characteristic times versus aquifer particularities.

Following Bolin and Rhode [7], some aquifer configuration particular cases can be drawn from the first moments of $\varphi(t)$ and $\psi(t)$.

The first considerations correspond to the case for which the average transit time and the average internal age are identical, $\tau_t = \tau_i$. Using Eqs. (45) and (46), the condition for having $\tau_t = \tau_0 = \tau_i$ is $\int_0^\infty t[\varphi(t) - \psi(t)]dt = 0$, for which a sufficient condition is $\varphi(t) = \psi(t) = \frac{1}{\tau_0} \exp\left(-\frac{t}{\tau_0}\right)$. The exponential form of the transit time pdf is a direct consequence of the first-order linear differential equation (42): if one of the two pdfs $\varphi(t)$ and $\psi(t)$ has an exponential form, then the other must be identical. This is the exponential model, often termed the well-mixed model, which is mathematically equivalent to the unit response function of a well-mixed reservoir. In chemical engineering, this model is used for reactors inside which the age distribution of the elements is uniform, i.e. there is a perfect mixing of the elements. Although the exponential model is widely used by hydrogeologists to simulate isotopic data, its application in aquifer systems must be handled carefully, since it involves

a large number of poorly realistic assumptions on the aquifer structure and recharge conditions. Eriksson [26] interpreted the exponential distribution of ages in groundwater as a consequence of an exponential decrease of porosity and permeability with depth. Luther and Haitjema [44] argued that the conditions on the validity of the exponential residence time distribution in porous media (horizontal, un-stratified and homogeneous aquifer with respect to porosity ϕ , recharge rate I , and saturated thickness H), can be relaxed if the parameters ϕ , I , and H vary in a piecewise constant way, such that the ratio $\phi H/I$ remains constant throughout the domain. This ratio characterizes the system turnover time, which means that each water sample taken from the reservoir must lead to a mean age that equals the aquifer mean turnover time. In nature however, such system configurations and conditions on mean age may hardly be found. Etcheverry [30] showed that a simple linear variation of the thickness H significantly influences the shape of the theoretical exponential residence time distribution.

We now consider the case where $\tau_t > \tau_i$. This case corresponds to the situation for which only few water molecules leave the aquifer rapidly after having entered. Confined aquifer conditions and/or very distant recharge and discharge zones are typical settings leading to these features. For such a configuration, the outlet transit time pdf $\varphi(t)$ is generally small or nil for young ages, attesting the existence of a minimum duration for travelling from inlet to outlet. The functions $v_A(t)$ and $M(t)$ tend to remain identical until the minimum transit time is reached. After this date, the function $v_A(t)$ should decrease rapidly, reflecting the fact that after the shortest travel distance from source to sink has been covered, the outflow of older water molecules is concentrated over a short time-span, in relation to the relative uniformity of the travel distances within the system. A narrow triangle-shaped function $v_A(t)$ is typical of aquifers with significant minimum transit times and bad turnover property. Note also that from Eq. (46) one can see that for systems with large turnover time, or relatively low hydro-dispersive properties (i.e. when $\sigma[\varphi]$ is small), the average age in the reservoir may also be smaller than the turnover time, with the lowest possible value $\tau_i = \frac{\tau_0}{2}$ for the piston-flow configuration only ($\sigma[\varphi] = 0$).

Finally, the case $\tau_t < \tau_i$ corresponds to the situation for which important amounts of water molecules enter the aquifer and flow out relatively rapidly, while sufficient amounts of water stay long enough to increase the value of τ_i . For such a configuration, $\varphi(0)$ must be bigger than $\psi(0)$, and the two curves must both decrease and cross each other at a certain date, after which $\psi(t)$ is higher than $\varphi(t)$. This situation may be encountered when the source and sink zones are close to each other, or when superficial recharge is uniformly distributed, such that the fraction of young water is important at outlet, but when the heterogeneity of the velocity distribution is such that long travel paths might lead to old ages within the domain. Karstic systems are typical media where the case $\tau_t < \tau_i$ is encountered, in relation to the effect of the

high velocities in the karstic network, which can carry water molecules more or less independently of the surrounding low permeability matrix. Considering Eq. (46), the case $\tau_t < \tau_i$ can occur in systems with small turnover time, or relatively high hydro-dispersive properties (large $\sigma[\varphi]$).

5 Analysis of dispersion and aquifer geometry effects on age distributions.

In the following, 2-D theoretical examples are presented to illustrate the proposed methods. Analytical and numerical solutions are provided in order to test the sensitivity of the probability and density functions to the advective and dispersive parameters, as well as to the aquifer structure.

5.1 Two-dimensional single flow system aquifer.

A 2-D half-circular crown-shaped reservoir is used to simulate a single-flow system aquifer, homogeneous with respect to porosity ϕ and hydraulic conductivity K . A positive head difference is applied between the recharge and discharge areas (Fig. 7a). This geometry is well suited for the derivation of analytical solutions [29]. Due to homogeneity and symmetry, the flow lines remain parallel to each other, flow being one-dimensional along the flow line coordinate. The spatial distributions of mean age and mean life expectancy can thus be solved analytically (see Appendix B), and reveal to be symmetric (Fig. 7a), yielding a co-central distribution of mean transit time. The porous volumes v_A ($= v_{A1} + v_{A2}$) and v_T ($= v_{T1} + v_{T2}$), quantified using the cumulative outflow function $F(t)$, can easily be identified in Fig. 7 by using the mean age and the mean transit time isochrones. Note that the special case of this theoretical aquifer allows a good representation of the groundwater internal volumes with the mean values of the global distributions. However, the mean of the age, life expectancy, and transit time distributions would generally give a rough representation only, when e.g. significant dispersive processes take place. Etcheverry and Perrochet [29] analyzed the pure advective case and found that $\varphi(t)$ is proportional to $1/t$, and that $\psi(t)$ is proportional to $\ln(1/t)$ between the minimum and the maximum transit time (see Fig. 8a). The function $\Psi(t)$ is a constant from the minimum to the maximum transit time, which indicates that the aquifer volumes ranging between a unit increase of transit time remain constant (the aquifer volumes between two iso-contours in Fig. 7b are all the same). The case $\alpha_T = 0$ in Fig. 8a was analyzed by means of analytical solutions (Appendix B). For this system, the pdfs $\varphi(t)$, $\psi(t)$ and $\Psi(t)$ show generally moderate fluctuations with respect to longitudinal dispersion. The main effect of the α_L coefficient can be seen in the increase of the spread-

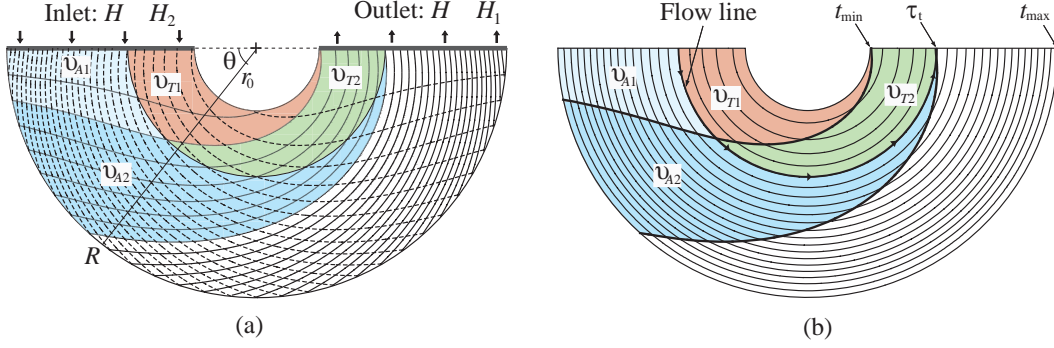


Fig. 7. Analytical solutions for mean age, mean life expectancy and mean transit time for the 2-D vertical half-circular aquifer (Appendix B): (a) Mean age (solid lines) and mean life expectancy (dashed lines) isochrones with 50 days increment; (b) Mean transit time isochrones with 50 days increment. Parameters: $\Delta H = H_2 - H_1 = 100$ m, $K = 10^{-4}$ m/s, $\phi = 0.2$, inner radius $r_0 = 250$ m, outer radius $R = 1000$ m, minimum transit time $t_{\min} = 143$ days, maximum transit time $t_{\max} = 2285$ days, turnover time $\tau_0 = \tau_t = 772.5$ days.

ing of the probability distributions. The outlet transit time pdf shows younger arrival times when α_L increases, but also a longer tail. The functions $\psi(t)$ and $\Psi(t)$ are affected the same way by longitudinal dispersion. The average internal age τ_i and the average internal transit time τ_{it} are dispersion dependent; they increase linearly with α_L , indicating that dispersion leads to a higher average age of the system. Note that the second temporal moments of the internal age and transit time distributions increase proportionally with the square of α_L , while the variance of $\varphi(t)$ increases linearly with α_L . Contrasted behavior appears when the coupled effect of longitudinal and lateral dispersivity is taken into account (Fig. 8b). The case $\alpha_T \neq 0$ was analyzed using numerical solutions, by increasing the ratio $\alpha = \alpha_L/\alpha_T$. The tailing effect decreases from a starting situation ($\alpha = \infty$ in Fig. 8b) with increasing values of lateral dispersivity (decrease of α ratio in Fig. 8b). Lateral dispersivity induces the mixing of ages, old water molecules moving laterally between the flow lines and replacing younger molecules, and vice-versa. The internal groundwater volume functions also attest of the above-mentioned dispersion effects. For example, the function $v_A(t)$ shows long tails for large values of α_L , reinforcing the observed behavior at outlet of the transit time pdf for old ages. The internal increase of water volumes that require long transit times to exit the aquifer due to an increase of α_L has of course its consequence at outlet with older arrival times. As with the pdfs $\varphi(t)$, $\psi(t)$ and $\Psi(t)$, this tailing effect decreases when lateral dispersion is added.

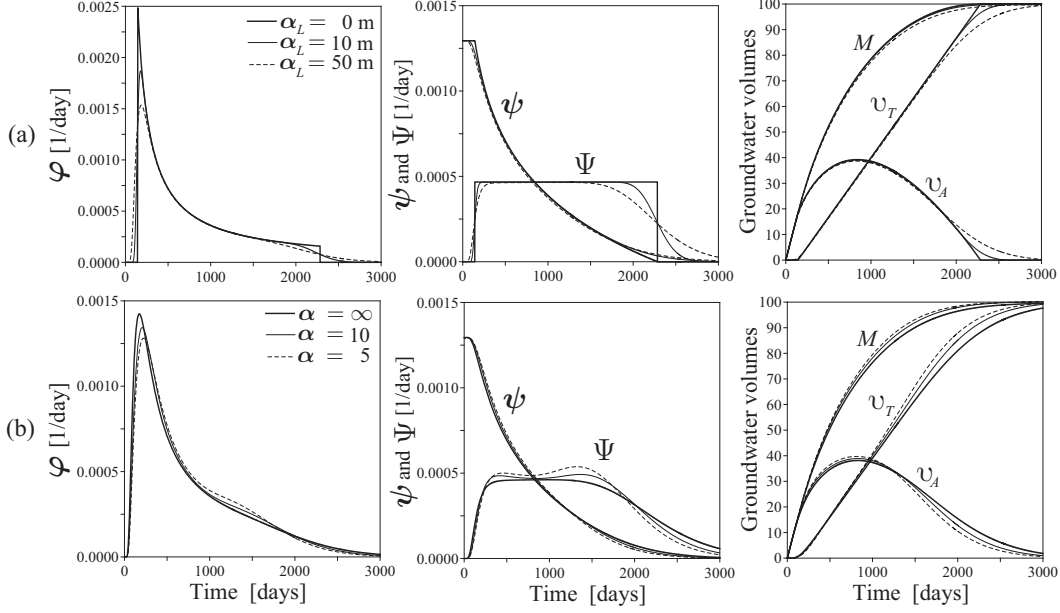


Fig. 8. RT solutions for the 2-D vertical half-circular aquifer: (a) Analytical solutions (see Appendix B) for the pdfs $\varphi(t)$, $\psi(t)$ and $\Psi(t)$, and for the internal groundwater volume functions (in % of M_0) $M(t)$, $v_A(t)$ and $v_T(t)$, as a function of the α_L coefficient ($\alpha_T = D_m = 0$); (b) Numerical solutions as a function of the ratio $\alpha = \alpha_L / \alpha_T$, with $\alpha_L = 50$ m.

5.2 Vertical multi-layer aquifer.

In this second theoretical example, we consider a four-layered vertical aquifer system, as illustrated in Fig. 9a. From the top to the bottom of the model, the layers have decreasing thicknesses and increasing pore velocities. The domain is discretized into 30'000 homogeneous bilinear quadrangles. The total porous volume M_0 is 65312.5 m³. A constant input flow rate enters the system along the left limit, using imposed fluxes of varying intensity proportional to the different layers hydraulic conductivities. The system turnover time is $\tau_0 = 162.267$ days. The outlet is simulated at the top of the right side by a constant hydraulic head along a relative small zone of 15 m. The permeability-porosity couples have been set in a way that the pore velocity contrasts involve specific ages within each layer (velocities v_i in Fig. 9a), creating specific ages within each layer, as illustrated in Fig. 9b. The fact that the layers thickness diminishes with depth, while the influx intensity increases, is meant to create arrival time peaks at outlet of comparable orders of magnitude. The temporal moments τ_i and τ_{it} are good indicators of the dynamics of the global system. Because they are volume-averaged quantities, their magnitude will depend on the water quantities of contrasted age and transit time, which are directly related to the flow and transport dynamics. For this example, τ_i and τ_{it} show only small variations with respect to dispersion (Table 1), because even if velocities between layers are contrasted, flow in the system is generally

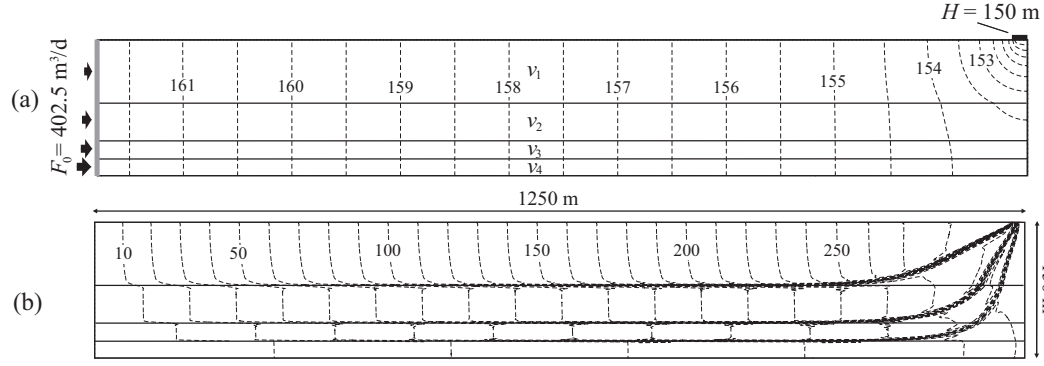


Fig. 9. 2-D vertical multi-layered aquifer: (a) Boundary conditions and Laplacian flow field in meters; (b) Mean age isochrones in days, illustrating the pore velocity contrast effect on age transport ($\alpha_L = \Delta x = \Delta z = 2.5$ m, $\alpha_T = 0$, $D_m = 0$). Average pore velocities (in m/day): $v_1 = 4.0$, $v_2 = 6.5$, $v_3 = 10.5$, $v_4 = 23.5$.

rapid. Longitudinal dispersion has the effect of making the system older, by creating long tails that can be observed at the reservoir outlet, but also on the internal age and internal transit time distributions (Figs. 10a and 10b). Spreading in the direction of velocity is of course the main cause for this. Lateral dispersion presents the property of homogenizing the ages by mixing water molecules of different ages. For a given level of longitudinal dispersion, increasing the ratio $\alpha = \alpha_L/\alpha_T$ (Fig. 11) makes the system younger (tailing is lowered), with diminishing values of the mean internal age τ_i and the mean internal transit time τ_{it} (Table 1). Longitudinal dispersion induces spreading of solute particles, and thus variability around the plume center of gravity. When lateral dispersion is added, the mixing of water molecules between flow lines homogenizes the ages. When longitudinal spreading is important, the exchange surface along the plume body is extended, and mixing can then be expected to be of high magnitude. The internal transit time pdf $\Psi(t)$ is of particular interest for the characterization of the internal organization of the flow dynamics. Its shape and particularly the number of modes it shows has a direct consequence on the shape of the outlet transit time pdf. If we take the example of the case $\alpha = \infty$ ($\alpha_T = 0$) in Fig. 11, the function $\Psi(t)$ exhibits as many peaks as the outlet transit time pdf $\varphi(t)$. However, the magnitude of these peaks are different for the two functions, and discern the transit time frequencies at outlet from those of the system pore volume. The peak of maximum intensity is the first one for $\varphi(t)$, and the third one for $\Psi(t)$. If one looks at the time value corresponding to the first peak of $\varphi(t)$, say t_1 , then inside the domain the density of probability that the water molecules have a transit time equal to t_1 is smaller than the same density of probability at the reservoir outlet. This is due to the fact that $\Psi(t)$ deals with volume-average probabilities while $\varphi(t)$ deals with flux-average probabilities. The four consecutive peaks of the outlet transit time pdf correspond to the four families of water molecules, which transit within the four layers of the system, even though some parts of the curve attest to some mixing effects (the density of

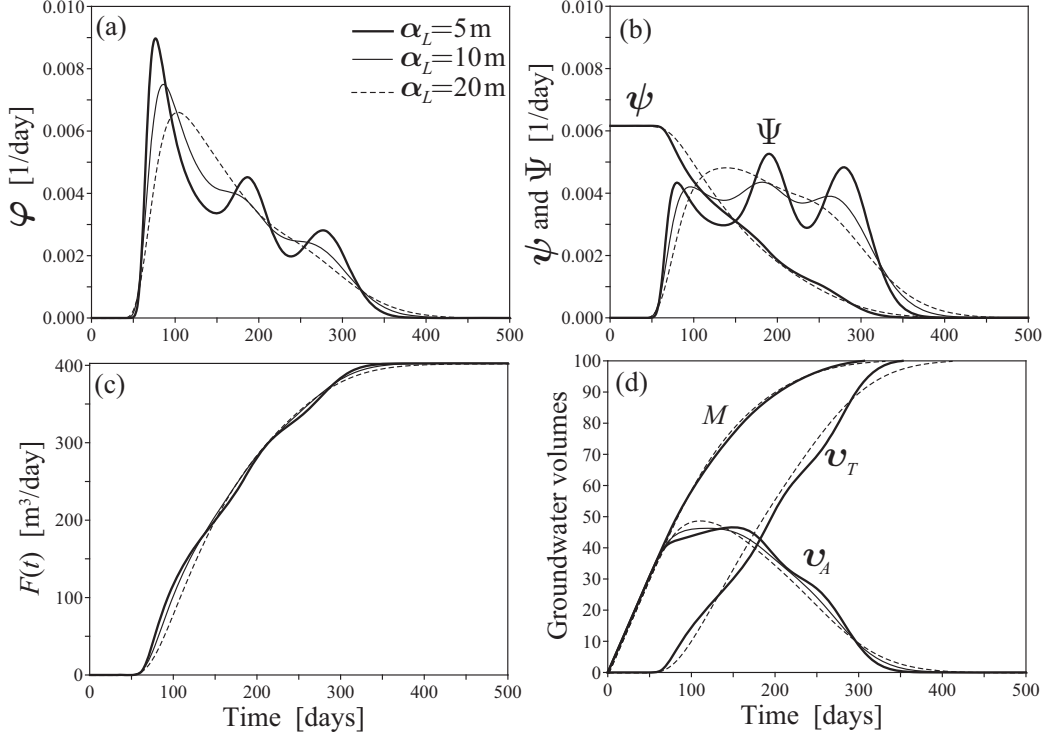


Fig. 10. Calculated pdfs, cdfs and groundwater volumes for the 2-D vertical multi-layered aquifer as a function of dispersion, for the ratio $\alpha = \alpha_L/\alpha_T = 10$: (a) Outlet transit time pdf; (b) Internal age pdf and internal transit time pdf; (c) Outlet cumulated outflow function; (d) Groundwater volumes versus time (in % of M_0).

Table 1

Dispersive parameters related to Figs. 10 and 11, and calculated pdf statistics (units in meters and days).

Parameters	Fig. 10			Fig. 11		
$\alpha = \alpha_L/\alpha_T$	10	10	10	∞	50	10
α_L	5.0	10.0	20.0	5.0	5.0	5.0
α_T	0.5	1.0	2.0	0.0	0.1	0.5
Statistics						
$\sigma[\varphi]$	75.710	75.955	79.871	81.766	79.786	75.940
τ_1	98.902	98.915	101.010	102.156	100.905	98.916

probability is not necessarily zero between two peaks). This simple theoretical example shows the complexity that is to be expected for the nature of the age and transit time distributions. It underlines how the significance of average age can lead to erroneous interpretations, regarding the system dynamics (e.g. inferences on average velocity) or hydrogeological problems related to risk and vulnerability assessment. Whenever the outlet transit time pdf is multi-modal,

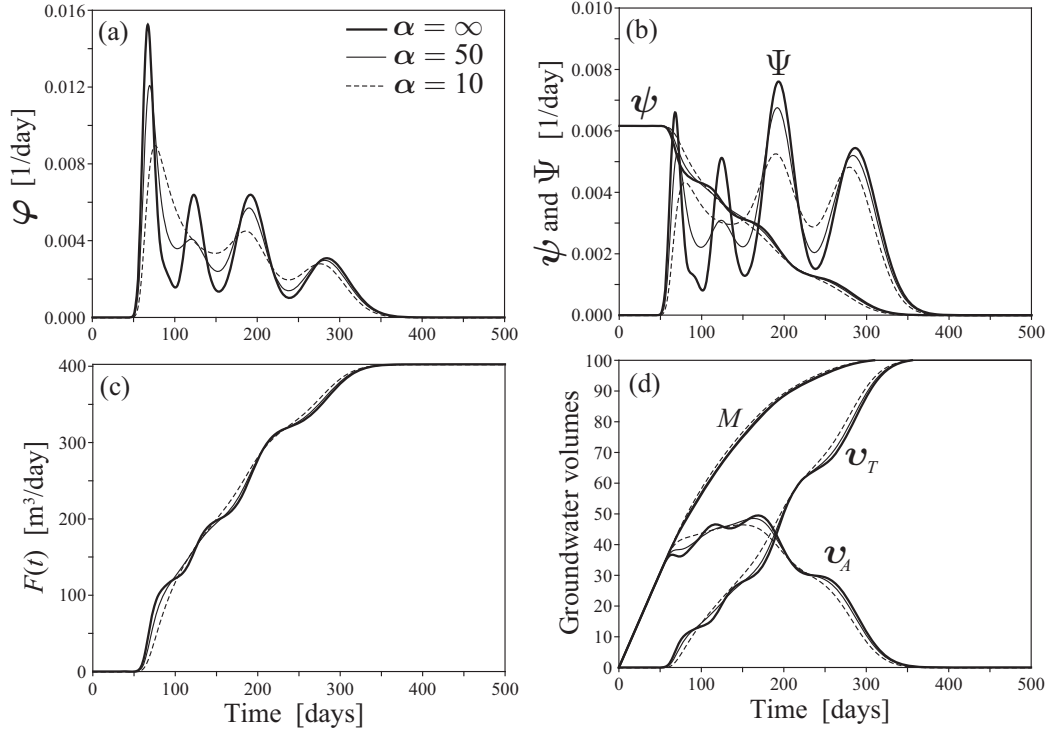


Fig. 11. Calculated pdfs, cdfs and groundwater volumes for the 2-D vertical multi-layered aquifer as a function of the ratio $\alpha = \alpha_L / \alpha_T$: (a) Outlet transit time pdf; (b) Internal age pdf and internal transit time pdf; (c) Outlet cumulated outflow function; (d) Groundwater volumes versus time (in % of M_0).

then the average transit time can definitely not be used as a reliable quantity representative of the distribution since, as illustrated here, mean ages at outlet are mostly related to the lowest densities of probability (see Figs. 10 and 11, Table 1). Once more this consideration points out to the interpretation of average age measurements, but also mean age simulations, which should be done very carefully. Generally, attention is given to hydrodynamic dispersion, heterogeneity, and long distance travelling induced mixing [35,71,72], which are factors that represent a source of uncertainty for the age dating methods and environmental tracer data interpretations. Here one can see that the geological, the structural and the hydraulic boundary configurations can by themselves be responsible of unrepresentative mean ages, even in advection-dominated transport regimes. Even if the entire groundwater age distribution cannot be measured in the field, mean age dates can be of great help for model calibration purposes. However, mean ages should a priori not represent an absolute simulation answer, and the knowledge of the entire age distribution should be of prime interest in most cases.

6 Summary and conclusions.

(1) The probability distributional evolution of groundwater age and life expectancy has been simulated by forward and backward transient advection-dispersion type equations, according to proper boundary conditions. For a given position in space, the age and the life expectancy pdfs are complementary distributions. Straight application of the principle of superposition to these distributions results in an integrated distribution of transit times, which characterizes the probability of having a given transit time from the recharge zone to the discharge zone, together with the quantities associated to that transit time. The transit time pdf is simply the convolution integral of the age pdf and the life expectancy pdf, and tells about the entire history of water molecules since recharge until discharge. Age, life expectancy, and transit time pdfs provide different kind of information, and each of them can reveal to be more advantageous than the other one depending on the hydrogeological insights to be provided. For instance, life expectancy and transit time distributions are well suited for vulnerability assessment problems (e.g. well-head protection, or underground storage of toxic waste), and they allow the mapping of different regions within a recharge zone, in terms of residence time in the aquifer and associated properties.

(2) The results of Eriksson [27] have been recovered by manipulating the advection-dispersion equation, extending thus the RT to systems with significant dispersive components. In the classical RT neither advection nor dispersion was considered. We have demonstrated here that the RT is still valid in systems with spatially varying velocity fields and non-negligible dispersive/diffusive effects. The RT is a simple one-dimensional formulation, time being the only dependent variable. The outlet transit time distribution is derived from the internal age distribution, and therefore has a much more refined resolution. In so doing, mixing of converging flow patterns near the outlet is ignored, and the maximum transit time is never smaller than the maximum age in the reservoir. The RT formulation also applies to the internal distribution of life expectancy, and can be used to evaluate recharge zones life expectancy pdfs. It has also been shown that the RT can be expressed in a more compact form, which relates the outlet transit time distribution to its internal counterpart, the internal distribution of transit times from inlet to outlet.

(3) From the reservoir characteristic distributions, fundamental additional transient information on water volumes and water fluxes can be gained. From the outlet transit time cdf, specific groundwater porous volumes can directly be identified and quantified with respect to age, life expectancy and transit time. These functions can be very useful for aquifer characterization and intrinsic vulnerability assessments. They can be used to easily evaluate the magnitudes of young and old groundwater volumes in the aquifer.

(4) Using analytical and numerical solutions for theoretical aquifer configurations, some effects of macro-dispersion on simulated age and transit time distributions could be underlined. For instance, longitudinal dispersion can have a significant aging effect, while lateral dispersion rejuvenates the system through transverse mixing. Like in previous studies, it has been shown that the average age resulting from dating-methods, or direct simulations, can lead to erroneous interpretations. It is a well-known fact that dispersion can induce a high variability of the age distribution around the average. Here we have shown that not only the mixing processes could make the average age insignificant, but also the geological structure and the geometry of the flow patterns.

(5) The proposed methodology can equivalently be implemented in one-, two- and three-dimensions, and has considerable technical and numerical advantages, which may be pivotal in handling very large systems. In fact, when the outlet transit time pdf is defined by integrating all hydro-dispersive properties over the entire flow field, the level of refinement required by a stable transport model is generally sufficient. The RT ensures that the minimum and the maximum age in the reservoir are captured at the outlet, which is hardly the case with traditional methods, mainly because of the mixing of converging fluxes near the outlet. In the present work, the RT has been combined with ADEs, and the equations were solved using the LTG technique. However, no restriction appears for the use of the methodology if age and life expectancy pdfs are calculated by other transport models, such as random-walk simulators.

(6) The presented models have been developed for the global aquifer system, regardless the number of individual inlet and outlet zones. At this stage, the RT has been rendered applicable to the whole system. In a subsequent article (this issue), we generalize the RT to any observation zone, and to systems with several inlets and outlets.

Acknowledgements

The authors would like to acknowledge the Swiss Research National Fund for financially supporting this research under Grant no. 2100-064927. The authors also thank Professor H.-J. Diersch and one anonymous reviewer for constructive criticism of this manuscript.

Appendix A: Reservoir Theory for a 1-D semi-infinite domain.

The age resident pdf is found by solving the one-dimensional form of the age pdf ADE (2a) with the Cauchy type condition $vg_A(0, t) - D\partial g_A(0, t)/\partial x = v\delta(t)$, and with a zero concentration gradient at a point at infinity. The corresponding age flux pdf is the flux concentration g_A^f , which is deduced using the one-dimensional form of Eq. (7), $g_A^f = g_A - \frac{D}{v} \frac{\partial g_A}{\partial x}$. These solutions are e.g. given in Jury and Roth [39]. Using the dimensionless variables

$$X = \frac{x}{L} \quad T = \frac{v}{L}t \quad \text{Pe} = \frac{vL}{D}$$

where L is a characteristic length defining the supposed outlet position, and where Pe is the Péclet number, the age resident and flux pdfs read

$$g_A(X, T) = \frac{\sqrt{\text{Pe}}}{\sqrt{\pi T}} \exp\left(-\frac{\text{Pe}(X - T)^2}{4T}\right) - \frac{\text{Pe}}{2} \exp(X\text{Pe}) \text{erfc}\left(\frac{\sqrt{\text{Pe}}(X + T)}{2\sqrt{T}}\right) \quad (\text{A.1})$$

$$g_A^f(X, T) = \frac{X\sqrt{\text{Pe}}}{2\sqrt{\pi T^{\frac{3}{2}}}} \exp\left(-\frac{\text{Pe}(X - T)^2}{4T}\right) \quad (\text{A.2})$$

The life expectancy resident and flux pdfs can be deduced from (A.1) and (A.2) by substitution of X by $1 - X$ and X by 1 , respectively:

$$g_E(X, T) = \frac{\sqrt{\text{Pe}}}{\sqrt{\pi T}} \exp\left(-\frac{\text{Pe}(1 - X - T)^2}{4T}\right) - \frac{\text{Pe}}{2} \exp[(1 - X)\text{Pe}] \text{erfc}\left(\frac{\sqrt{\text{Pe}}(1 - X + T)}{2\sqrt{T}}\right) \quad (\text{A.3})$$

$$g_E^f(X, T) = \frac{(1 - X)\sqrt{\text{Pe}}}{2\sqrt{\pi T^{\frac{3}{2}}}} \exp\left(-\frac{\text{Pe}(1 - X - T)^2}{4T}\right) \quad (\text{A.4})$$

The transit time flux pdf is calculated by straight application in the time domain of the convolution integral in Eq. (12):

$$\begin{aligned} g_T^f(X, T) &= \int_0^T g_A^f(X, T') g_E^f(X, T - T') dT' = \frac{\sqrt{\text{Pe}}}{2\sqrt{\pi T^{\frac{3}{2}}}} \exp\left(-\frac{\text{Pe}(1 - T)^2}{4T}\right) \\ &= g_A^f(1, T) = g_E^f(0, T) \end{aligned} \quad (\text{A.5})$$

The transit time flux pdf in Eq. (A.5) could have been deduced by substitution of X by 1 in Eq. (A.2), or by substitution of X by 0 in Eq. (A.4). The transit time resident pdf is found by convoluting (A.1) and (A.3) in the Laplace

domain:

$$\hat{g}_T(X, s) = \hat{g}_A(X, s)\hat{g}_E(X, s) = \frac{4}{(1 + \gamma)^2} \exp\left(\frac{\text{Pe}}{2} [1 - \gamma]\right) \quad (\text{A.6})$$

where s is the Laplace variable, \hat{g} is s -transformed state of the function g , and with $\gamma = \sqrt{(1 + 4s/\text{Pe})}$. The inversion of Eq. (A.6) yields

$$\begin{aligned} g_T(X, T) &= g_T(T) \\ &= \text{Pe} \left(1 + \frac{\text{Pe}(1 + T)}{2}\right) \exp(\text{Pe}) \text{erfc}\left(\frac{\text{Pe}(1 + T)}{2\sqrt{\text{Pe}T}}\right) \\ &\quad - \frac{\text{Pe}^2 T}{\sqrt{\pi \text{Pe}T}} \exp\left(-\frac{\text{Pe}(1 - T)^2}{4T}\right) \end{aligned} \quad (\text{A.7})$$

where use has been made of the shifting theorem

$$\mathcal{L}^{-1}\{f(as + b)\} = \frac{e^{-\frac{bt}{a}}}{a} f\left(\frac{t}{a}\right),$$

and of the following Laplace transform:

$$\begin{aligned} \mathcal{L}^{-1}\left\{\frac{\exp(-c\sqrt{s})}{(b + \sqrt{s})^2}\right\} &= (1 + bc + 2b^2t) \exp(b^2t + bc) \text{erfc}\left(\frac{c}{2\sqrt{t}} + b\sqrt{t}\right) \\ &\quad - \frac{2bt}{\sqrt{\pi t}} \exp\left(-\frac{c^2}{4t}\right) \end{aligned}$$

The internal age, internal life expectancy and internal transit time pdfs are obtained from Eqs. (25), (27) and (29):

$$\begin{aligned} \psi(T) &= \int_0^1 g_A(X, T) dX = \int_0^1 g_E(X, T) dX \\ &= \frac{1}{2} \left(\text{erfc}\left(\frac{\sqrt{\text{Pe}}(T - 1)}{2\sqrt{T}}\right) - \exp(\text{Pe}) \text{erfc}\left(\frac{\sqrt{\text{Pe}}(T + 1)}{2\sqrt{T}}\right) \right) \end{aligned} \quad (\text{A.8})$$

$$\Psi(T) = \int_0^1 g_T(X, T) dX = g_T(T) \quad (\text{A.9})$$

In 1-D, the reservoir theory is equivalent to the mass conservation relation between flux and resident concentrations given by Jury and Roth [39]:

$$\begin{aligned} \varphi(T) &= -\frac{\partial \psi(T)}{\partial T} = -\frac{\partial}{\partial T} \int_0^1 g(X, T) dX = \frac{\sqrt{\text{Pe}}}{2\sqrt{\pi}T^{\frac{3}{2}}} \exp\left(-\frac{\text{Pe}(1 - T)^2}{4T}\right) \\ &= g_A^f(1, T) = g_E^f(0, T) \end{aligned} \quad (\text{A.10})$$

The dimensionless outlet transit time pdf is simply the age flux concentration at $X = 1$, or equivalently the life expectancy flux concentration at $X = 0$. The mean of the pdfs $\varphi(T)$, $\psi(T)$, and $\Psi(T)$ read

$$\tau_t = \mu_1[\varphi] = 1 \quad \tau_i = \mu_1[\psi] = \frac{1}{2} + \frac{1}{\text{Pe}} \quad \tau_{it} = \mu_1[\Psi] = 1 + \frac{2}{\text{Pe}} = 2\tau_i \quad (\text{A.11})$$

and the spreading of these pdfs is measured by their variance:

$$\sigma^2[\varphi] = \frac{2}{\text{Pe}} \quad \sigma^2[\psi] = \frac{(\text{Pe}+6)^2}{12\text{Pe}^2} \quad \sigma^2[\Psi] = \frac{2\text{Pe}+6}{\text{Pe}^2} \quad (\text{A.12})$$

Appendix B: Reservoir Theory in a single flow system.

Consider the crown-shaped aquifer geometry in Fig. 7. Since the flow lines remain parallel to each other in the entire domain, we assume a 1-D transport process at each point $x = \theta r$ on the flow line coordinate. We follow the same procedure than in Appendix A, given that the porous volume is $M_0 = \phi\pi(R^2 - r_0^2)/2$, the steady flow rate $F_0 = K\Delta H \ln(R/r_0)/\pi$, the dispersion coefficient $D(r) = \alpha_L v(r)$, and the pore velocity $v(r) = q(r)/\phi = K\Delta H/\phi\pi r$. The age resident and flux pdfs are deduced from Eqs. (A.1) and (A.2) by substituting x by θr , and the life expectancy resident and flux pdfs are deduced by replacing x by $(\pi - \theta)r$. The transit time flux pdf is finally obtained by replacing x by πr in Eq. (A.2). The average age, life expectancy and transit time are given by the first moment of the corresponding flux pdfs:

$$\langle A \rangle(\theta, r) = \frac{\theta\phi\pi r^2}{K\Delta H} \quad (\text{B.1})$$

$$\langle E \rangle(\theta, r) = \frac{(\pi - \theta)\phi\pi r^2}{K\Delta H} \quad (\text{B.2})$$

$$\langle T \rangle(r) = \langle A \rangle(\theta, r) + \langle E \rangle(\theta, r) = \frac{\phi\pi^2 r^2}{K\Delta H} \quad (\text{B.3})$$

Since on the outlet line ($\theta = \pi$) velocity points in the direction of the outward unit vector, the discharge zone transit time pdf $\varphi(t)$ can be evaluated by averaging the age flux pdfs on the outlet line, or equivalently by averaging the life expectancy flux pdfs on the inlet line ($\theta = 0$). The internal age (or life expectancy) pdf $\psi(t)$, and the internal transit time pdf $\Psi(t)$ are calculated following the domain integration in Eqs. (25), (27) and (29), by integrating between the inner radius r_0 and the outer radius R , and by integrating between 0 and π (see Fig. 7). The average transit time τ_t equals the turnover time τ_0 (see Eq. (45)):

$$\tau_t = \tau_0 = \frac{M_0}{F_0} = \frac{\phi\pi^2(R^2 - r_0^2)}{2K\Delta H \ln(R/r_0)} \quad (\text{B.4})$$

The average internal age (or life expectancy) τ_i and internal transit time $\tau_{it} = 2\tau_i$ vary linearly with α_L :

$$\tau_i = \mu_1[\psi] = \frac{\phi\pi}{12K\Delta H(R^2 - r_0^2)}[8(R^3 - r_0^3)\alpha_L + 3\pi(R^4 - r_0^4)] \quad (\text{B.5})$$

The variance of $\varphi(t)$ can then be deduced from Eqs. (B.4) and (B.5) by enforcing Eq. (46).

References

- [1] Amin I. E., Campana M. E. A general lumped parameter model for the interpretation of tracer data and transit time calculation in hydrologic systems. *J Hydrol* 1996;179:1-21.
- [2] Arnold L. *Stochastic Differential Equations: Theory and Applications*. New York: John Wiley, 1974.
- [3] Bear J. *Dynamics of Fluids in Porous Media*. New York: Elsevier, 1972.
- [4] Bear J., Verruitj A. *Modeling Groundwater Flow and Pollution*. Boston: D. Reidel, 1987.
- [5] Benjamin J. R., Cornell C. A. *Probability, Statistics, and Decision for Civil Engineers*. New York: McGraw-Hill Book Co.; 1970.
- [6] Boehlke J. K., Denver J. M. Combined use of groundwater dating, chemical, and isotopic analysis to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland. *Water Resour Res* 1996;31(9):2319-2339.
- [7] Bolin B., Rodhe H. A note on the concept of age distribution and transit time in natural reservoirs. *Tellus XXV* 1973;1:58-62.
- [8] Busenberg E., Plummer L. N. Use of chlorofluoromethanes (CCL3F and CCL2F2) as hydrologic tracers and age-dating tools; The alluvium and terrace system of central Oklahoma. *Water Resour Res* 1992;28(9):2257-2283.
- [9] Campana M. E., Simpson E. Groundwater residence times and recharge rates using a discrete-state compartment model and ^{14}C data. *J Hydrol* 1984;72:171-185.
- [10] Campana M. E. Generation of Ground-Water Age Distributions. *Ground Water* 1987;25(1):51-58.
- [11] Cook P. G., Solomon D. K. Recent advances in dating young groundwater: chlorofluorocarbons, $^3\text{H}/^3\text{He}$ and ^{85}Kr . *J Hydrol* 1997;191:245-265.
- [12] Cordes C., Kinzelbach W. Continuous groundwater velocity fields and path lines in linear, bilinear, and trilinear finite elements. *Water Resour Res* 1992;28:2903-2911.

- [13] Cornaton F. Deterministic models of groundwater age, life expectancy and transit time distributions in advective–dispersive systems. Ph.D. thesis, University of Neuchâtel, Switzerland, 2003.
- [14] Cornaton F., Perrochet P., Diersch H.-J. G. A finite element formulation of the outlet gradient boundary condition for convective–diffusive transport problems. *Int J Numer Meth Engng* 2004;61:2716-2732.
- [15] Crump K. S. Numerical Inversion of Laplace Transforms Using Fourier Series Approximation. *J Ass Comp Mech* 1976;23(1):89-96.
- [16] Dagan G. Stochastic modelling of groundwater flow by unconditional and conditional probabilities, 2, The solute transport. *Water Resour Res* 1982;18(4):835-848.
- [17] Dagan G. Solute transport in heterogeneous porous formations. *J Fluid Mech* 1984;145:151-177.
- [18] Dagan G. Theory of solute transport by groundwater. *Ann Rev Fluid Mech* 1987;19:183-215.
- [19] Dagan G. *Flow and Transport in Porous Formations*. Berlin, Heidelberg, Germany:Springer, 1989.
- [20] Dagan G., Nguyen V. A comparison of travel time and concentration approaches to modelling transport by groundwater. *J Contam Hydrol* 1989;4:79-91.
- [21] Danckwerts P. V. Continuous flow systems: distribution of residence times. *Chemical engineering science* 1953;2(1):93-102.
- [22] Davis S. N., Bentley H. W. Dating groundwater, a short review, In *Nuclear and Chemical Dating Techniques*:Lloyd Curie, Am. Chem. Soc. Symp. Ser. 1982;176:187-222.
- [23] Diersch H.-J. G. About the difference between the convective and the divergence form of the transport equation. *FEFLOW Software White Papers Vol.I*, 1998, WASY GmbH Berlin.
- [24] De Hoog F. R., Knight J. H., Stokes A. N. An improved method for numerical inversion of Laplace transforms. *SIAM J Sci Stat Comput* 1982;3:357-366.
- [25] Dunkle S. A., Plummer L. N., Busenberg E., Phillips P. J., Denver J. M., Hamilton P. A., Michel R. L., Coplen T. B. Chlorofluorocarbons (CCl₃F and ClC₁₂F₂) as dating tools and hydrologic tracers in shallow groundwater of the Delmarva Peninsula, Atlantic Coastal Plain, United States. *Water Resour Res* 1993;29:3837–3860.
- [26] Eriksson E. The possible use of Tritium for estimating groundwater storage. *Tellus* 1958;10:472–478.
- [27] Eriksson E. Compartment models and reservoir theory. *Annual Review of Ecology and Systematics* 1971;2:67-84.

- [28] Etcheverry D., Perrochet P. Reservoir theory, groundwater transit time distributions and lumped parameter models. IAEA–SM–361/44, Vienna, 1999.
- [29] Etcheverry D., Perrochet P. Direct simulation of groundwater transit time distributions using the reservoir theory. *Hydrogeology Journal* 2000;8:200-208.
- [30] Etcheverry D. Une approche déterministe des distributions des temps de transit de l'eau souterraine par la théorie des réservoirs. Ph.D. thesis, University of Neuchâtel, Switzerland, 2001.
- [31] Frind E. Solution of the Advection-Dispersion Equation with Free Exit Boundary. *Numer Meth Partial Diff Eqs* 1988;4:301–313.
- [32] Garabedian P. R. Partial Differential Equations. New York: John Wiley, 1964.
- [33] Gardiner C. W. Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences. Berlin: Springer, 1983.
- [34] Gelhar L. W., Axness C. L. Three-dimensional stochastic analysis of macro dispersion in aquifers. *Water Resour Res* 1983;19(1):161-180.
- [35] Goode D. J. Direct simulation of groundwater age. *Water Resour Res* 1996;32:289-296.
- [36] Haitjema H. M. On the residence time distributions in idealized groundwatersheds. *J Hydrol* 1995;172:127-146.
- [37] Harvey C. F., Gorelick S. M. Temporal moment generating equations: Modeling transport and mass transfer in heterogeneous aquifers. *Water Resour Res* 1995;31:1895-1912.
- [38] Jury W. A. Simulation of Solute transport Using a Transfer Function Model. *Water Resour Res* 1982;18(2):363-368.
- [39] Jury W. A., Roth K. Transfer Functions and Solute Transport Through Soil: Theory and Applications. Basel: Birkhauser Publ., 1990.
- [40] Kolmogorov A. N. Über die analytischen Methoden in der Wahrscheinlichkeitsrechnung. *Math Anal* 1931;104:415–458.
- [41] Kreft A., Zuber A. On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. *Chem Eng Sci* 1978;33:1471-1480.
- [42] Kreft A., Zuber A. Comments on "Flux-Averaged and Volume-Averaged Concentrations in Continuum Approaches to Solute Transport" by J. C. Parker and M. Th. van Genuchten. *Water Resour Res* 1986;22(7):1157-1158.
- [43] LaBolle E. M., Quastel J., Fogg G. E. Diffusion theory for transport in porous media: Transition-probability densities of diffusion processes corresponding to advection–dispersion equations. *Water Resour Res* 1998;34(7):1685-1693.
- [44] Luther K. H., Haitjema H. M. Numerical experiments on the residence time distributions of heterogeneous groundwatersheds. *J Hydrol* 1998;207:1-17.

- [45] Maloszewski P., Zuber A. Determining the turnover time of groundwater systems with the aid of environmental tracers, 1, Models and their applicability. *J Hydrol* 1982;57:207-231.
- [46] Maloszewski P., Zuber A. Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate aquifers. *Water Resour Res* 1991;27:1937-1945.
- [47] Maloszewski P., Zuber A. Principles and practice of calibration and validation of mathematical models for the interpretation of environmental tracer data in aquifers. *Adv Water Res* 1993;16:173-190.
- [48] Nauman E. B., Buffham B. A. *Mixing in Continuous Flow Systems*. New York:John Wiley, 1983.
- [49] Neumann S. P., Winter C. L., Newman C. M. Stochastic theory of field-scale Fickian dispersion in anisotropic porous media. *Water Resour Res* 1987;23:453-466.
- [50] Neupauer R., Wilson J. L. Adjoint method for obtaining backward-in-time location and travel time probabilities of a conservative groundwater contaminant. *Water Resour Res* 1999;35(11):3389-3398.
- [51] Neupauer R., Wilson J. L. Adjoint-derived location and travel time probabilities for a multidimensional groundwater system. *Water Resour Res* 2001;37(6):1657-1668.
- [52] Neupauer R., Wilson J. L. Backward probabilistic model of groundwater contamination in non-uniform and transient flow. *Adv Water Res* 2002;25:733-746.
- [53] Parker J. C., van Genuchten M. Th. Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport. *Water Resour Res* 1984;20(7):866-872.
- [54] Parker J. C., van Genuchten M. Th. Reply. *Water Resour Res* 1986;22(7):1159-1160.
- [55] Plummer L. N., Michel R. L., Thurman E. M., Glynn P. D. Environmental tracers for age dating young ground water. In *Regional ground-water quality 1993*, New York:Alley W. M., Van Nostrand Reinhold, 255–294.
- [56] Reilly T. E., Plummer L. N., Phillips P. J., Busenberg E. The use of simulation and multiple environmental tracers to quantify groundwater flow in a shallow aquifer. *Water Resour Res* 1994;30:421-433.
- [57] Richter J., Szymezak P., Abraham T., Jordan H. Use of combination of lumped parameter models to interpret groundwater isotopic data. *J Contam Hydrol* 1993;14(1):1-13.
- [58] Robertson W. D., Cherry J. A. Tritium as an indicator of recharge and dispersion in a groundwater system in Central Ontario. *Water Resour Res* 1989;25:1097-1109.

- [59] Rubin Y. Applied Stochastic Hydrology. New York: Oxford University Press; 2003.
- [60] Shapiro A. M., Cvetkovic V. D. Stochastic analysis of solute arrival time in heterogeneous porous media. *Water Resour Res* 1988;24(10):1711-1718.
- [61] Saad Y., Schultz M. GMRES: A generalized minimal residual algorithm for solving nonsymmetric linear systems. *SIAM J Sci Statist Comput* 1986;7:856–869.
- [62] Saad Y. ILUT: A dual threshold incomplete ILU factorization. *Linear Algebra Appl* 1994;1:387-402.
- [63] Solomon D. K., Poreda R. J., Schiff S. L., Cherry J. A. Tritium and Helium 3 as groundwater-age tracers in the Borden aquifer. *Water Resour Res* 1992;28:741–755.
- [64] Spalding D. B. A note on mean residence-times in steady flows of arbitrary complexity. *Chem Eng Sci* 1958;9:74-77.
- [65] Sposito G., Barry D. A. On the Dagan model of solute transport in groundwater: Foundational aspects. *Water Resour Res* 1987;23(10):1867-1875.
- [66] Sudicky E. A., Frind E. Carbon 14 dating of groundwater in confined aquifers: Implication of aquitard diffusion. *Water Resour Res* 1981;17:1060-1064.
- [67] Sudicky E. A. A natural-gradient experiment on solute transport in a sand aquifer: spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resour Res* 1986;22:2069-2082.
- [68] Sudicky E. A. The Laplace transform Galerkin technique: A time-continuous finite element theory and application to mass transport in groundwater. *Water Resour Res* 1989;25(8):1833-1846.
- [69] Uffink G. J. M. Application of the Kolmogorovs backward equation in random walk simulation of groundwater contaminant transport. In *Contaminant Transport in Groundwater*. Balkema, Rotterdam:H. E. Kobus and Kinzelbach, 1989.
- [70] van der Vorst H. A. Bi-CGSTAB: A fast and smoothly converging variant of Bi-CG for the solution of non-symmetric linear systems. *SIAM J Sci Statist Comput* 1992;12:631–644.
- [71] Varni M., Carrera J. Simulation of groundwater age distributions. *Water Resour Res* 1998;34(12):3271-3281.
- [72] Weissmann G. S., Zhang Y., LaBolle E., Fogg G. E. Dispersion of groundwater age in an alluvial aquifer system. *Water Resour Res* 2002;38(10):doi:10.1029/2001WR000907.
- [73] Wilson J. L., Liu J. Field Validation of the Backward-in-Time Advection Dispersion Theory. In *Proceedings of the 1996 HSRC/WERC Joint Conference on the Environment, Great Plains-Rocky Mountain Hazard*. Substance Cent., Manhattan, Kansas, 1997.

- [74] Zuber A. Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. In Handbook of Environmental Isotope Geochemistry 2:Fritz P. and Fontes J. -Ch, 1986.